

## Section IV

### ORGANIC MOLECULAR FUNCTIONAL GROUPS AND MOLECULES

5 Organic molecules comprising an arbitrary number of atoms can be solved using the similar principles and procedures as those used to solve alkanes of arbitrary length. Alkanes can be considered to be comprised of the functional groups of  $CH_3$ ,  $CH_2$ , and  $C - C$ . These groups with the corresponding geometrical parameters and energies can be added as a linear sum to give the solution of any straight chain alkane as shown in the Continuous-Chain Alkanes  
10 section. Similarly, the geometrical parameters and energies of all functional groups such as alkanes, branched alkanes, alkenes, branched alkenes, alkynes, alkyl fluorides, alkyl chlorides, alkyl bromides, alkyl iodides, alkene halides, primary alcohols, secondary alcohols, tertiary alcohols, ethers, primary amines, secondary amines, tertiary amines, aldehydes, ketones, carboxylic acids, carboxylic esters, amides, N-alkyl amides, N,N-dialkyl amides,  
15 urea, acid halides, acid anhydrides, nitriles, thiols, sulfides, disulfides, sulfoxides, sulfones, sulfites, sulfates, nitro alkanes, nitrites, nitrates, conjugated polyenes, aromatics, heterocyclic aromatics, substituted aromatics, and others can be solved. The functional-group solutions can be made into a linear superposition and sum, respectively, to give the solution of any organic molecule. The solutions of the functional groups can be conveniently obtained by  
20 using generalized forms of the geometrical and energy equations. The equations and sections that are referenced by not contained in this text refer to those sections and equations of the book by R. L. Mills entitled, "The Grand Unified Theory of Classical Quantum Mechanics", June 2006 Edition, Cadmus Professional Communications-Science Press Division, Ephrata, PA, ISBN 0963517171, Library of Congress Control Number 2005936834; posted at  
25 <http://www.blacklightpower.com/bookdownload.shtml> which is incorporated in its entirety by reference.

Consider the case wherein at least two atomic orbital hybridize as a linear combination of electrons at the same energy in order to achieve a bond at an energy minimum, and the sharing of electrons between two or more such orbitals to form a MO  
30 permits the participating hybridized orbitals to decrease in energy through a decrease in the radius of one or more of the participating orbitals. The force generalized constant  $k'$  of a

$H_2$ -type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by:

$$k' = \frac{C_1 C_2 2e^2}{4\pi\epsilon_0} \quad (15.1)$$

where  $C_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the molecule or molecular ion which is 0.75 (Eq. (13.59)) in the case of  $H$  bonding to a central atom and 0.5 (Eq. (14.152)) otherwise, and  $C_2$  is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of the chemical bond. From Eqs. (13.58-13.63), the distance from the origin of the MO to each focus  $c'$  is given by:

$$c' = a \sqrt{\frac{\hbar^2 4\pi\epsilon_0}{m_e e^2 2C_1 C_2 a}} = \sqrt{\frac{a a_0}{2C_1 C_2}} \quad (15.2)$$

10 The internuclear distance is

$$2c' = 2 \sqrt{\frac{a a_0}{2C_1 C_2}} \quad (15.3)$$

The length of the semiminor axis of the prolate spheroidal MO  $b = c$  is given by

$$b = \sqrt{a^2 - c'^2} \quad (15.4)$$

And, the eccentricity,  $e$ , is

$$15 \quad e = \frac{c'}{a} \quad (15.5)$$

From Eqs. (11.207-11.212), the potential energy of the two electrons in the central field of the nuclei at the foci is

$$V_e = n_1 c_1 c_2 \frac{-2e^2}{8\pi\epsilon_0 \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} \quad (15.6)$$

The potential energy of the two nuclei is

$$20 \quad V_p = n_1 \frac{e^2}{8\pi\epsilon_0 \sqrt{a^2 - b^2}} \quad (15.7)$$

The kinetic energy of the electrons is

$$T = n_1 c_1 c_2 \frac{\hbar^2}{2m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} \quad (15.8)$$

And, the energy,  $V_m$ , of the magnetic force between the electrons is

$$V_m = n_1 c_1 c_2 \frac{-\hbar^2}{4m_e a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} \quad (15.9)$$

The total energy of the  $H_2$ -type prolate spheroidal MO,  $E_T(H_2MO)$ , is given by the sum of the energy terms:

$$E_T(H_2MO) = V_e + T + V_m + V_p \quad (15.10)$$

$$\begin{aligned} E_T(H_2MO) &= -\frac{n_1 e^2}{8\pi\epsilon_0 \sqrt{a^2 - b^2}} \left[ c_1 c_2 \left( 2 - \frac{a_0}{a} \right) \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} - 1 \right] \\ &= -\frac{n_1 e^2}{8\pi\epsilon_0 c'} \left[ c_1 c_2 \left( 2 - \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] \end{aligned} \quad (15.11)$$

where  $n_1$  is the number of equivalent bonds of the MO and applies in the case of functional groups. In the case of independent MOs not in contact with the bonding atoms, the terms based on charge are multiplied by  $c_{BO}$ , the bond-order factor. It is 1 for a single bond, 4 for an independent double bond as in the case of the  $CO_2$  and  $NO_2$  molecules, and 9 for an independent triplet bond. Then, the kinetic energy term is multiplied by  $c'_{BO}$  which is 1 for a single bond, 2 for a double bond, and 9/2 for a triple bond.  $c_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of an MO which is 0.75 (Eqs. (13.67-13.73)) in the case of  $H$  bonding to an unhybridized central atom and 1 otherwise, and  $c_2$  is the factor that results in an equipotential energy match of the participating the MO and the at least two atomic orbitals of the chemical bond. Specifically, to meet the equipotential condition and energy matching conditions for the union of the  $H_2$ -type-ellipsoidal-MO and the HOs or AOs of the bonding atoms, the factor  $c_2$  of a  $H_2$ -type ellipsoidal MO may given by (i) one, (ii) the ratio of the Coulombic or valence energy of the AO or HO of at least one atom of the bond and 13.605804 eV, the Coulombic energy between the electron and proton of  $H$ , (iii) the ratio of the valence energy of the AO or HO of one atom and the Coulombic energy of another, (iv) the ratio of the valence energies of the AOs or HOs of two atoms, (v) the ratio of two  $c_2$  factors corresponding to any of cases (ii)-(iv), and (vi) the product of two different  $c_2$  factors corresponding to any of the cases (i)-(v). Specific examples of the factor  $c_2$  of a  $H_2$ -type ellipsoidal MO given in previous sections are

0.936127, the ratio of the ionization energy of  $N$  14.53414 eV and 13.605804 eV, the Coulombic energy between the electron and proton of  $H$ ;

448

0.91771, the ratio of 14.82575 eV,  $-E_{Coulomb}(C, 2sp^3)$ , and 13.605804 eV ;

0.87495, the ratio of 15.55033 eV,  $-E_{Coulomb}(C_{ethane}, 2sp^3)$ , and 13.605804 eV ;

0.85252, the ratio of 15.95955 eV,  $-E_{Coulomb}(C_{ethylene}, 2sp^3)$ , and 13.605804 eV ;

0.85252, the ratio of 15.95955 eV,  $-E_{Coulomb}(C_{benzene}, 2sp^3)$ , and 13.605804 eV, and

5 0.86359, the ratio of 15.55033 eV,  $-E_{Coulomb}(C_{alkane}, 2sp^3)$ , and 13.605804 eV .

In the generalization of the hybridization of at least two atomic-orbital shells to form a shell of hybrid orbitals, the hybridized shell comprises a linear combination of the electrons of the atomic-orbital shells. The radius of the hybridized shell is calculated from the total Coulombic energy equation by considering that the central field decreases by an integer for  
10 each successive electron of the shell and that the total energy of the shell is equal to the total Coulombic energy of the initial AO electrons. The total energy  $E_T(atom, msp^3)$  ( $m$  is the integer of the valence shell) of the AO electrons and the hybridized shell is given by the sum of energies of successive ions of the atom over the  $n$  electrons comprising total electrons of the at least one AO shell.

$$15 \quad E_T(atom, msp^3) = -\sum_{m=1}^n IP_m \quad (15.12)$$

where  $IP_m$  is the  $m$ th ionization energy (positive) of the atom. The radius  $r_{msp^3}$  of the hybridized shell is given by:

$$r_{msp^3} = \sum_{q=Z-n}^{Z-1} \frac{-(Z-q)e^2}{8\pi\epsilon_0 E_T(atom, msp^3)} \quad (15.13)$$

Then, the Coulombic energy  $E_{Coulomb}(atom, msp^3)$  of the outer electron of the  $atom msp^3$   
20 shell is given by

$$E_{Coulomb}(atom, msp^3) = \frac{-e^2}{8\pi\epsilon_0 r_{msp^3}} \quad (15.14)$$

In the case that during hybridization at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy  $E(magnetic)$  at the initial radius  $r$  of the AO electron:

$$25 \quad E(magnetic) = \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 r^3} = \frac{8\pi\mu_0 \mu_B^2}{r^3} \quad (15.15)$$



Then, the energy  $E(atom, msp^3)$  of the outer electron of the  $atom msp^3$  shell is given by the sum of  $E_{Coulomb}(atom, msp^3)$  and  $E(magnetic)$ :

$$E(atom, msp^3) = \frac{-e^2}{8\pi\epsilon_0 r_{msp^3}} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 r^3} \quad (15.16)$$

Consider next that the at least two atomic orbitals hybridize as a linear combination of 5 electrons at the same energy in order to achieve a bond at an energy minimum with another atomic orbital or hybridized orbital. As a further generalization of the basis of the stability of the MO, the sharing of electrons between two or more such hybridized orbitals to form a MO permits the participating hybridized orbitals to decrease in energy through a decrease in the radius of one or more of the participating orbitals. In this case, the total energy of the 10 hybridized orbitals is given by the sum of  $E(atom, msp^3)$  and the next energies of successive ions of the atom over the  $n$  electrons comprising the total electrons of the at least two initial AO shells. Here,  $E(atom, msp^3)$  is the sum of the first ionization energy of the atom and the hybridization energy. An example of  $E(atom, msp^3)$  for  $E(C, 2sp^3)$  is given in Eq. (14.503) where the sum of the negative of the first ionization energy of  $C$ ,  $-11.27671 eV$ , plus the 15 hybridization energy to form the  $C2sp^3$  shell given by Eq. (14.146) is  $E(C, 2sp^3) = -14.63489 eV$ .

Thus, the sharing of electrons between two  $atom msp^3$  HOs to form an atom-atom-bond MO permits each participating hybridized orbital to decrease in radius and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each  $atom msp^3$  20 HO donates an excess of 25% per bond of its electron density to the atom-atom-bond MO to form an energy minimum wherein the atom-atom bond comprises one of a single, double, or triple bond. In each case, the radius of the hybridized shell is calculated from the Coulombic energy equation by considering that the central field decreases by an integer for each successive electron of the shell and the total energy of the shell is equal to the total 25 Coulombic energy of the initial AO electrons plus the hybridization energy. The total energy  $E_T(mol.atom, msp^3)$  ( $m$  is the integer of the valence shell) of the HO electrons is given by the sum of energies of successive ions of the atom over the  $n$  electrons comprising total electrons of the at least one initial AO shell and the hybridization energy:

450

$$E_T(\text{mol.atom}, msp^3) = E(\text{atom}, msp^3) - \sum_{m=2}^n IP_m \quad (15.17)$$

where  $IP_m$  is the  $m$ th ionization energy (positive) of the atom and the sum of  $-IP_1$  plus the hybridization energy is  $E(\text{atom}, msp^3)$ . Thus, the radius  $r_{msp^3}$  of the hybridized shell is given by:

$$5 \quad r_{msp^3} = \left( \sum_{q=Z-n}^{Z-1} (Z-q) - s(0.25) \right) \frac{-e^2}{8\pi\epsilon_0 E_T(\text{mol.atom}, msp^3)} \quad (15.18)$$

where  $s = 1, 2, 3$  for a single, double, and triple bond, respectively. The Coulombic energy  $E_{Coulomb}(\text{mol.atom}, msp^3)$  of the outer electron of the  $\text{atom } msp^3$  shell is given by

$$E_{Coulomb}(\text{mol.atom}, msp^3) = \frac{-e^2}{8\pi\epsilon_0 r_{msp^3}} \quad (15.19)$$

In the case that during hybridization at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy  $E(\text{magnetic})$  at the initial radius  $r$  of the AO electron given by Eq. (15.15). Then, the energy  $E(\text{mol.atom}, msp^3)$  of the outer electron of the  $\text{atom } msp^3$  shell is given by the sum of  $E_{Coulomb}(\text{mol.atom}, msp^3)$  and  $E(\text{magnetic})$ :

$$E(\text{mol.atom}, msp^3) = \frac{-e^2}{8\pi\epsilon_0 r_{msp^3}} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 r^3} \quad (15.20)$$

15  $E_T(\text{atom} - \text{atom}, msp^3)$ , the energy change of each  $\text{atom } msp^3$  shell with the formation of the atom-atom-bond MO is given by the difference between  $E(\text{mol.atom}, msp^3)$  and  $E(\text{atom}, msp^3)$ :

$$E_T(\text{atom} - \text{atom}, msp^3) = E(\text{mol.atom}, msp^3) - E(\text{atom}, msp^3) \quad (15.21)$$

As examples from prior sections,  $E_{Coulomb}(\text{mol.atom}, msp^3)$  is one of:

$$20 \quad E_{Coulomb}(C_{\text{ethylene}}, 2sp^3), \quad E_{Coulomb}(C_{\text{ethane}}, 2sp^3), \quad E_{Coulomb}(C_{\text{acetylene}}, 2sp^3), \quad \text{and} \\ E_{Coulomb}(C_{\text{alkane}}, 2sp^3);$$

$E_{Coulomb}(\text{atom}, msp^3)$  is one of  $E_{Coulomb}(C, 2sp^3)$  and  $E_{Coulomb}(Cl, 3sp^3)$ ;

451

$E(\text{mol. atom}, msp^3)$  is one of  $E(C_{ethylene}, 2sp^3)$ ,  $E(C_{ethane}, 2sp^3)$ ,  $E(C_{acetylene}, 2sp^3)$ ,  $E(C_{alkane}, 2sp^3)$ ;

$E(\text{atom}, msp^3)$  is one of and  $E(C, 2sp^3)$  and  $E(Cl, 3sp^3)$ ;

$E_T(\text{atom} - \text{atom}, msp^3)$  is one of  $E(C - C, 2sp^3)$ ,  $E(C = C, 2sp^3)$ , and  $E(C \equiv C, 2sp^3)$ ;

5

$\text{atom } msp^3$  is one of  $C2sp^3$ ,  $Cl3sp^3$

$E_T(\text{atom} - \text{atom}(s_1), msp^3)$  is  $E_T(C - C, 2sp^3)$  and  $E_T(\text{atom} - \text{atom}(s_2), msp^3)$  is  $E_T(C = C, 2sp^3)$ , and

$r_{msp^3}$  is one of  $r_{C2sp^3}$ ,  $r_{ethane2sp^3}$ ,  $r_{ethylene2sp^3}$ ,  $r_{acetylene2sp^3}$ ,  $r_{alkane2sp^3}$ , and  $r_{Cl3sp^3}$ .

In the case of the  $C2sp^3$  HO, the initial parameters (Eqs. (14.142-14.146)) are

$$10 \quad r_{2sp^3} = \sum_{n=2}^5 \frac{(Z-n)e^2}{8\pi\epsilon_0 (e148.25751 \text{ eV})} = \frac{10e^2}{8\pi\epsilon_0 (e148.25751 \text{ eV})} = 0.91771a_0 \quad (15.22)$$

$$E_{Coulomb}(C, 2sp^3) = \frac{-e^2}{8\pi\epsilon_0 r_{2sp^3}} = \frac{-e^2}{8\pi\epsilon_0 0.91771a_0} = -14.82575 \text{ eV} \quad (15.23)$$

$$E(\text{magnetic}) = \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 (r_3)^3} = \frac{8\pi\mu_0 \mu_B^2}{(0.84317a_0)^3} = 0.19086 \text{ eV} \quad (15.24)$$

$$\begin{aligned} E(C, 2sp^3) &= \frac{-e^2}{8\pi\epsilon_0 r_{2sp^3}} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 (r_3)^3} \\ &= -14.82575 \text{ eV} + 0.19086 \text{ eV} \\ &= -14.63489 \text{ eV} \end{aligned} \quad (15.25)$$

In Eq. (15.18),

$$15 \quad \sum_{q=Z-n}^{Z-1} (Z-q) = 10 \quad (15.26)$$

Eqs. (14.147) and (15.17) give

$$E_T(\text{mol. atom}, msp^3) = E_T(C_{ethane}, 2sp^3) = -151.61569 \text{ eV} \quad (15.27)$$

Using Eqs. (15.18-15.28), the final values of  $r_{C2sp^3}$ ,  $E_{Coulomb}(C2sp^3)$ , and  $E(C2sp^3)$ , and the resulting  $E_T(C - C, C2sp^3)$  of the MO due to charge donation from the HO to the MO where

$C-C$  refers to the bond order of the carbon-carbon bond for different values of the parameter  $s$  are given in Table 15.1.

Table 15.1. The final values of  $r_{C2sp^3}$ ,  $E_{Coulomb}(C2sp^3)$ , and  $E(C2sp^3)$  and the resulting  
 5  $E_T\left(C-C, C2sp^3\right)$  of the MO due to charge donation from the HO to the MO where  $C-C$   
 refers to the bond order of the carbon-carbon bond.

| MO<br>Bond Order<br>(BO) | $s$ 1 | $s$ 2 | $r_{C2sp^3}(a_0)$<br>Final | $E_{Coulomb}(C2sp^3)$<br>(eV)<br>Final | $E(C2sp^3)$<br>(eV)<br>Final | $E_T\left(C-C, C2sp^3\right)$<br>(eV) |
|--------------------------|-------|-------|----------------------------|----------------------------------------|------------------------------|---------------------------------------|
| I                        | 1     | 0     | 0.87495                    | -15.55033                              | -15.35946                    | -0.72457                              |
| II                       | 2     | 0     | 0.85252                    | -15.95955                              | -15.76868                    | -1.13379                              |
| III                      | 3     | 0     | 0.83008                    | -16.39089                              | -16.20002                    | -1.56513                              |
| IV                       | 4     | 0     | 0.80765                    | -16.84619                              | -16.65532                    | -2.02043                              |

In another generalized case of the basis of forming a minimum-energy bond with the constraint that it must meet the energy matching condition for all MOs at all HOs or AOs, the  
 10 energy  $E(mol.atom, msp^3)$  of the outer electron of the  $atom msp^3$  shell of each bonding atom must be the average of  $E(mol.atom, msp^3)$  for two different values of  $s$ :

$$E(mol.atom, msp^3) = \frac{E(mol.atom(s_1), msp^3) + E(mol.atom(s_2), msp^3)}{2} \quad (15.28)$$

In this case,  $E_T(atom - atom, msp^3)$ , the energy change of each  $atom msp^3$  shell with the formation of each atom-atom-bond MO, is average for two different values of  $s$ :

$$15 \quad E_T(atom - atom, msp^3) = \frac{E_T(atom - atom(s_1), msp^3) + E_T(atom - atom(s_2), msp^3)}{2} \quad (15.29)$$

Consider an aromatic molecule such as benzene given in the Benzene Molecule section. Each  $C=C$  double bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from two sets of two  $C2sp^3$  HOs of the participating carbon atoms. Each  $C-H$  bond of  $CH$  having two spin-paired electrons, one from an initially  
 20 unpaired electron of the carbon atom and the other from the hydrogen atom, comprises the

linear combination of 75%  $H_2$ -type ellipsoidal MO and 25%  $C2sp^3$  HO as given by Eq. (13.439). However,  $E_T(atom - atom, msp^3)$  of the  $C-H$ -bond MO is given by  $0.5E_T(C = C, 2sp^3)$  (Eq. (14.247)) corresponding to one half of a double bond that matches the condition for a single-bond order for  $C-H$  that is lowered in energy due to the aromatic character of the bond.

A further general possibility is that a minimum-energy bond is achieved with satisfaction of the potential, kinetic, and orbital energy relationships by the formation of an MO comprising an allowed multiple of a linear combination of  $H_2$ -type ellipsoidal MOs and corresponding HOs or AOs that contribute a corresponding allowed multiple (e.g. 0.5, 0.75, 1) of the bond order given in Table 15.1. For example, the alkane MO given in the Continuous-Chain Alkanes section comprises a linear combination of factors of 0.5 of a single bond and 0.5 of a double bond.

Consider a first MO and its HOs comprising a linear combination of bond orders and a second MO that shares a HO with the first. In addition to the mutual HO, the second MO comprises another AO or HO having a single bond order or a mixed bond order. Then, in order for the two MOs to be energy matched, the bond order of the second MO and its HOs or its HO and AO is a linear combination of the terms corresponding to the bond order of the mutual HO and the bond order of the independent HO or AO. Then, in general,  $E_T(atom - atom, msp^3)$ , the energy change of each  $atom\ msp^3$  shell with the formation of each atom-atom-bond MO, is a weighted linear sum for different values of  $s$  that matches the energy of the bonded MOs, HOs, and AOs:

$$E_T(atom - atom, msp^3) = \sum_{n=1}^N c_{s_n} E_T(atom - atom(s_n), msp^3) \quad (15.30)$$

where  $c_{s_n}$  is the multiple of the BO of  $s_n$ . The radius  $r_{msp^3}$  of the  $atom\ msp^3$  shell of each bonding atom is given by the Coulombic energy using the initial energy  $E_{Coulomb}(atom, msp^3)$  and  $E_T(atom - atom, msp^3)$ , the energy change of each  $atom\ msp^3$  shell with the formation of each atom-atom-bond MO:

$$r_{msp^3} = \frac{-e^2}{8\pi\epsilon_0\alpha_0 (E_{Coulomb}(atom, msp^3) + E_T(atom - atom, msp^3))} \quad (15.31)$$

where  $E_{Coulomb}(C2sp^3) = -14.825751 \text{ eV}$ . The Coulombic energy  $E_{Coulomb}(mol.atom,msp^3)$  of the outer electron of the  $atom\ msp^3$  shell is given by Eq. (15.19). In the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy  $E(magnetic)$  (Eq. (15.15)) at the initial radius  $r$  of the AO electron. Then, the energy  $E(mol.atom,msp^3)$  of the outer electron of the  $atom\ msp^3$  shell is given by the sum of  $E_{Coulomb}(mol.atom,msp^3)$  and  $E(magnetic)$  (Eq. (15.20)).  $E_T(atom - atom,msp^3)$ , the energy change of each  $atom\ msp^3$  shell with the formation of the atom-atom-bond MO is given by the difference between  $E(mol.atom,msp^3)$  and  $E(atom,msp^3)$  given by Eq. (15.21). Using Eq. (15.23) for  $E_{Coulomb}(C,2sp^3)$  in Eq. (15.31), the single bond order energies given by Eqs. (15.18-15.27) and shown in Table 15.1, and the linear combination energies (Eqs. (15.28-15.30)), the parameters of linear combinations of bond orders and linear combinations of mixed bond orders are given in Table 15.2.

Table 15.2. The final values of  $r_{C2sp^3}$ ,  $E_{Coulomb}(C2sp^3)$ , and  $E(C2sp^3)$  and the resulting  $E_T\left(\overset{BO}{C} - C, C2sp^3\right)$  of the MO comprising a linear combination of  $H_2$ -type ellipsoidal MOs and corresponding HOs of single or mixed bond order where  $c_{s_n}$  is the multiple of the bond order parameter  $E_T(atom - atom(s_n),msp^3)$  given in Table 15.1.

Table 15.1

| MO<br>Bond<br>Order<br>(BO) | $s$<br>1 | $c_{s_1}$ | $s$<br>2 | $c_{s_2}$ | $s$<br>3 | $c_{s_3}$ | $r_{C2sp^3}(a_0)$<br>Final | $E_{Coulomb}(C2sp^3)$<br>(eV)<br>Final | $E(C2sp^3)$<br>(eV)<br>Final | $E_T\left(C - C, C2sp^3\right)$<br>(eV) |
|-----------------------------|----------|-----------|----------|-----------|----------|-----------|----------------------------|----------------------------------------|------------------------------|-----------------------------------------|
| 1/2I                        | 1        | 0.5       | 0        | 0         | 0        | 0         | 0.89582                    | -15.18804                              | -14.99717                    | -0.36228                                |
| 1/2II                       | 2        | 0.5       | 0        | 0         | 0        | 0         | 0.88392                    | -15.39265                              | -15.20178                    | -0.56689                                |
| I +                         | 1        | 0.5       | 2        | 0.2       | 0        | 0         | 0.87941                    | -15.47149                              | -15.28062                    | -0.64573                                |
| 1/2II                       |          |           |          | 5         |          |           |                            |                                        |                              |                                         |
| 1/2II                       | 2        | 0.2       | 1        | 0.2       | 2        | 0.2       | 0.87363                    | -15.57379                              | -15.38293                    | -0.74804                                |
| + (I +                      |          | 5         |          | 5         |          | 5         |                            |                                        |                              |                                         |
| II)                         |          |           |          |           |          |           |                            |                                        |                              |                                         |
| 3/4II                       | 2        | 0.7       | 0        | 0         | 0        | 0         | 0.86793                    | -15.67610                              | -15.48523                    | -0.85034                                |
|                             |          | 5         |          |           |          |           |                            |                                        |                              |                                         |
| I + II                      | 1        | 0.5       | 2        | 0.5       | 0        | 0         | 0.86359                    | -15.75493                              | -15.56407                    | -0.92918                                |
| I +                         | 1        | 0.5       | 3        | 0.5       | 0        | 0         | 0.85193                    | -15.97060                              | -15.77974                    | -1.14485                                |
| III                         |          |           |          |           |          |           |                            |                                        |                              |                                         |
| I +                         | 1        | 0.5       | 4        | 0.5       | 0        | 0         | 0.83995                    | -16.19826                              | -16.00739                    | -1.37250                                |
| IV                          |          |           |          |           |          |           |                            |                                        |                              |                                         |
| II +                        | 2        | 0.5       | 3        | 0.5       | 0        | 0         | 0.84115                    | -16.17521                              | -15.98435                    | -1.34946                                |
| III                         |          |           |          |           |          |           |                            |                                        |                              |                                         |
| II +                        | 2        | 0.5       | 4        | 0.5       | 0        | 0         | 0.82948                    | -16.40286                              | -16.21200                    | -1.57711                                |
| IV                          |          |           |          |           |          |           |                            |                                        |                              |                                         |
| III +                       | 3        | 0.5       | 4        | 0.5       | 0        | 0         | 0.81871                    | -16.61853                              | -16.42767                    | -1.79278                                |
| IV                          |          |           |          |           |          |           |                            |                                        |                              |                                         |
| IV +                        | 4        | 0.5       | 4        | 0.5       | 0        | 0         | 0.80765                    | -16.84619                              | -16.65532                    | -2.02043                                |
| IV                          |          |           |          |           |          |           |                            |                                        |                              |                                         |

Consider next the radius of the AO or HO due to the contribution of charge to more than one bond. The energy contribution due to the charge donation at each atom such as 5 carbon superimposes linearly. In general, the radius  $r_{mol2sp^3}$  of the  $C2sp^3$  HO of a carbon atom of a given molecule is calculated using Eq. (14.514) by considering  $\sum E_{T_{mol}}(MO, 2sp^3)$ , the total energy donation to each bond with which it participates in bonding. The general equation for the radius is given by

$$\begin{aligned}
 r_{mol2sp^3} &= \frac{-e^2}{8\pi\epsilon_0 \left( E_{Coulomb}(C, 2sp^3) + \sum E_{T_{mol}}(MO, 2sp^3) \right)} \\
 &= \frac{e^2}{8\pi\epsilon_0 \left( e14.825751 \text{ eV} + \sum E_{T_{mol}}(MO, 2sp^3) \right)}
 \end{aligned}
 \tag{15.32}$$

The Coulombic energy  $E_{Coulomb}(mol.atom, msp^3)$  of the outer electron of the  $atom msp^3$  shell is given by Eq. (15.19). In the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy  $E(magnetic)$  (Eq. (15.15)) at the initial radius  $r$  of the AO electron. Then, the energy  $E(mol.atom, msp^3)$  of the outer electron of the  $atom msp^3$  shell is given by the sum of  $E_{Coulomb}(mol.atom, msp^3)$  and  $E(magnetic)$  (Eq. (15.20)).

For example, the  $C2sp^3$  HO of each methyl group of an alkane contributes  $-0.92918 \text{ eV}$  (Eq. (14.513)) to the corresponding single  $C-C$  bond; thus, the corresponding  $C2sp^3$  HO radius is given by Eq. (14.514). The  $C2sp^3$  HO of each methylene group of  $C_nH_{2n+2}$  contributes  $-0.92918 \text{ eV}$  to each of the two corresponding  $C-C$  bond MOs. Thus, the radius (Eq. (15.32)), the Coulombic energy (Eq. (15.19)), and the energy (Eq. (15.20)) of each alkane methylene group are

$$\begin{aligned}
 r_{alkaneC_{methylene}2sp^3} &= \frac{-e^2}{8\pi\epsilon_0 \left( E_{Coulomb}(C, 2sp^3) + \sum E_{T_{alkane}}(methylene C-C, 2sp^3) \right)} \\
 &= \frac{e^2}{8\pi\epsilon_0 (e14.825751 \text{ eV} + e0.92918 \text{ eV} + e0.92918 \text{ eV})} \\
 &= 0.81549a_0
 \end{aligned}
 \tag{15.33}$$

$$E_{Coulomb}(C_{methylene}2sp^3) = \frac{-e^2}{8\pi\epsilon_0 (0.81549a_0)} = -16.68412 \text{ eV}
 \tag{15.34}$$

$$E(C_{methylene}2sp^3) = \frac{-e^2}{8\pi\epsilon_0 (0.81549a_0)} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 (0.84317a_0)^3} = -16.49325 \text{ eV}
 \tag{15.35}$$

In the determination of the parameters of functional groups, heteroatoms bonding to  $C2sp^3$  HOs to form MOs are energy matched to the  $C2sp^3$  HOs. Thus, the radius and the energy parameters of a bonding heteroatom are given by the same equations as those for



$C2sp^3$  HOs. Using Eqs. (15.15), (15.19-15.20), (15.24), and (15.32) in a generalized fashion, the final values of the radius of the HO or AO,  $r_{Atom.HO.AO}$ ,  $E_{Coulomb}(mol.atom,msp^3)$ , and  $E(C_{mol}2sp^3)$  are calculated using  $\sum E_{T_{group}}(MO,2sp^3)$ , the total energy donation to each bond with which an atom participates in bonding corresponding to the values of  $E_T\left(C^{BO}-C,C2sp^3\right)$  of

5 the MO due to charge donation from the AO or HO to the MO given in Tables 15.1 and 15.2.

Table 15.3.A. The final values of  $r_{Atom.HO.AO}$ ,  $E_{Coulomb}(mol.atom,msp^3)$ , and  $E(C_{mol}2sp^3)$  calculated using the values of  $E_T\left(C^{BO}-C,C2sp^3\right)$  given in Tables 15.1 and 15.2.

| Atom<br>Hybridiz<br>ation<br>Designat<br>ion | $E_r \left( C - C, C2sp^3 \right)^{BO}$ | $E_r \left( C - C, C2sp^3 \right)^{BO}$ | $E_r \left( C - C, C2sp^3 \right)^{BO}$ | $E_r \left( C - C, C2sp^3 \right)^{BO}$ | $E_r \left( C - C, C2sp^3 \right)^{BO}$ | $r_{Atom, HO, AO}$<br>Final | $E_{Condonb} (mol\ atom, msp^3)$<br>(eV)<br>Final | $E(C_{and} 2sp^3)$<br>(eV)<br>Final |
|----------------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------|---------------------------------------------------|-------------------------------------|
| 1                                            | 0                                       | 0                                       | 0                                       | 0                                       | 0                                       | 0.91771                     | -14.82575                                         | -14.63489                           |
| 2                                            | -0.36229                                | 0                                       | 0                                       | 0                                       | 0                                       | 0.89582                     | -15.18804                                         | -14.99717                           |
| 3                                            | -0.46459                                | 0                                       | 0                                       | 0                                       | 0                                       | 0.88983                     | -15.29034                                         | -15.09948                           |
| 4                                            | -0.56689                                | 0                                       | 0                                       | 0                                       | 0                                       | 0.88392                     | -15.39265                                         | -15.20178                           |
| 5                                            | -0.72457                                | 0                                       | 0                                       | 0                                       | 0                                       | 0.87495                     | -15.55033                                         | -15.35946                           |
| 6                                            | -0.85034                                | 0                                       | 0                                       | 0                                       | 0                                       | 0.86793                     | -15.6761                                          | -15.48523                           |
| 7                                            | -0.92918                                | 0                                       | 0                                       | 0                                       | 0                                       | 0.86359                     | -15.75493                                         | -15.56407                           |
| 8                                            | -0.54343                                | -0.54343                                | 0                                       | 0                                       | 0                                       | 0.85503                     | -15.91261                                         | -15.72175                           |
| 9                                            | -1.13379                                | 0                                       | 0                                       | 0                                       | 0                                       | 0.85252                     | -15.95955                                         | -15.76868                           |
| 10                                           | -1.14485                                | 0                                       | 0                                       | 0                                       | 0                                       | 0.85193                     | -15.9706                                          | -15.77974                           |
| 11                                           | -0.46459                                | -0.82688                                | 0                                       | 0                                       | 0                                       | 0.84418                     | -16.11722                                         | -15.92636                           |
| 12                                           | -1.34946                                | 0                                       | 0                                       | 0                                       | 0                                       | 0.84115                     | -16.17521                                         | -15.98435                           |
| 13                                           | -1.3725                                 | 0                                       | 0                                       | 0                                       | 0                                       | 0.83995                     | -16.19826                                         | -16.00739                           |
| 14                                           | -0.46459                                | -0.92918                                | 0                                       | 0                                       | 0                                       | 0.83885                     | -16.21952                                         | -16.02866                           |
| 15                                           | -0.72457                                | -0.72457                                | 0                                       | 0                                       | 0                                       | 0.836                       | -16.2749                                          | -16.08404                           |
| 16                                           | -0.5669                                 | -0.92918                                | 0                                       | 0                                       | 0                                       | 0.8336                      | -16.32183                                         | -16.13097                           |
| 17                                           | -0.82688                                | -0.72457                                | 0                                       | 0                                       | 0                                       | 0.83078                     | -16.37721                                         | -16.18634                           |
| 18                                           | -1.56513                                | 0                                       | 0                                       | 0                                       | 0                                       | 0.83008                     | -16.39089                                         | -16.20002                           |
| 19                                           | -0.64574                                | -0.92918                                | 0                                       | 0                                       | 0                                       | 0.82959                     | -16.40067                                         | -16.20981                           |
| 20                                           | -1.57711                                | 0                                       | 0                                       | 0                                       | 0                                       | 0.82948                     | -16.40286                                         | -16.212                             |
| 21                                           | -0.72457                                | -0.92918                                | 0                                       | 0                                       | 0                                       | 0.82562                     | -16.47951                                         | -16.28865                           |
| 22                                           | -0.85035                                | -0.85035                                | 0                                       | 0                                       | 0                                       | 0.82327                     | -16.52645                                         | -16.33559                           |
| 23                                           | -1.79278                                | 0                                       | 0                                       | 0                                       | 0                                       | 0.81871                     | -16.61853                                         | -16.42767                           |
| 24                                           | -1.13379                                | -0.72457                                | 0                                       | 0                                       | 0                                       | 0.81549                     | -16.68411                                         | -16.49325                           |
| 25                                           | -0.92918                                | -0.92918                                | 0                                       | 0                                       | 0                                       | 0.81549                     | -16.68412                                         | -16.49325                           |
| 26                                           | -2.02043                                | 0                                       | 0                                       | 0                                       | 0                                       | 0.80765                     | -16.84619                                         | -16.65532                           |

|    |          |          |          |          |   |         |           |           |
|----|----------|----------|----------|----------|---|---------|-----------|-----------|
| 27 | -1.13379 | -0.92918 | 0        | 0        | 0 | 0.80561 | -16.88872 | -16.69786 |
| 28 | -0.85035 | -0.85035 | -0.46459 | 0        | 0 | 0.80076 | -16.99104 | -16.80018 |
| 29 | -0.5669  | -0.72457 | -0.92918 | 0        | 0 | 0.78916 | -17.04641 | -16.85554 |
| 30 | -1.13379 | -1.13379 | 0        | 0        | 0 | 0.79597 | -17.09334 | -16.90248 |
| 31 | -1.34946 | -0.92918 | 0        | 0        | 0 | 0.79546 | -17.1044  | -16.91353 |
| 32 | -0.46459 | -0.92918 | -0.92918 | 0        | 0 | 0.79340 | -17.14871 | -16.95784 |
| 33 | -0.64574 | -0.85034 | -0.85034 | 0        | 0 | 0.79232 | -17.17217 | -16.98131 |
| 34 | -0.85035 | -0.5669  | -0.92918 | 0        | 0 | 0.79232 | -17.17218 | -16.98132 |
| 35 | -0.72457 | -0.72457 | -0.92918 | 0        | 0 | 0.79085 | -17.20408 | -17.01322 |
| 36 | -0.82688 | -0.72457 | -0.92918 | 0        | 0 | 0.78617 | -17.30638 | -17.11552 |
| 37 | -0.72457 | -0.92918 | -0.92918 | 0        | 0 | 0.78155 | -17.40868 | -17.21782 |
| 38 | -0.92918 | -0.72457 | -0.92918 | 0        | 0 | 0.78155 | -17.40869 | -17.21783 |
| 39 | -0.54343 | -0.54343 | -0.5669  | -0.92918 | 0 | 0.78155 | -17.40869 | -17.21783 |
| 40 | -0.92918 | -0.85034 | -0.85034 | 0        | 0 | 0.77945 | -17.45561 | -17.26475 |
| 41 | -0.82688 | -0.92918 | -0.92918 | 0        | 0 | 0.77699 | -17.51099 | -17.32013 |
| 42 | -0.92918 | -0.92918 | -0.92918 | 0        | 0 | 0.77247 | -17.6133  | -17.42244 |
| 43 | -0.85035 | -0.54343 | -0.5669  | -0.92918 | 0 | 0.76801 | -17.71561 | -17.52475 |
| 44 | -1.34946 | -0.64574 | -0.92918 | 0        | 0 | 0.76652 | -17.75013 | -17.55927 |
| 45 | -0.85034 | -0.54343 | -0.60631 | -0.92918 | 0 | 0.76631 | -17.75502 | -17.56415 |
| 46 | -1.1338  | -0.92918 | -0.92918 | 0        | 0 | 0.7636  | -17.81791 | -17.62705 |
| 47 | -0.46459 | -0.85035 | -0.85035 | -0.92918 | 0 | 0.75924 | -17.92022 | -17.72936 |
| 48 | -0.82688 | -1.34946 | -0.92918 | 0        | 0 | 0.75877 | -17.93128 | -17.74041 |
| 49 | -1.13379 | -1.13379 | -1.13379 | 0        | 0 | 0.74646 | -18.22712 | -18.03626 |
| 50 | -1.79278 | -0.92918 | -0.92918 | 0        | 0 | 0.73637 | -18.47690 | -18.28604 |

Table 15.3.B. The final values of  $r_{Atom.HO.AO}$ ,  $E_{Coulomb}(mol.atom,msp^3)$ , and  $E(C_{mol}2sp^3)$  calculated for heterocyclic groups using the values of  $E_T(C^{bo}-C,C2sp^3)$  given in Tables 15.1 and 15.2.

| Atom<br>Hybridization<br>Designation | $E_i \left( C - C, C2sp^3 \right)$ | $E_i \left( C - C, C2sp^3 \right)$ | $E_i \left( C - C, C2sp^3 \right)$ | $E_i \left( C - C, C2sp^3 \right)$ | $E_i \left( C - C, C2sp^3 \right)$ | $r_{Atom, HO, AO}$<br>Final | $E_{coulomb} (mol, atom, msp^3)$<br>(eV)<br>Final | $E(C_{mol} 2sp^3)$<br>(eV)<br>Final |
|--------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|-----------------------------|---------------------------------------------------|-------------------------------------|
| 1                                    | 0                                  | 0                                  | 0                                  | 0                                  | 0                                  | 0.91771                     | -14.82575                                         | -14.63489                           |
| 2                                    | -0.56690                           | 0                                  | 0                                  | 0                                  | 0                                  | 0.88392                     | -15.39265                                         | -15.20178                           |
| 3                                    | -0.72457                           | 0                                  | 0                                  | 0                                  | 0                                  | 0.87495                     | -15.55033                                         | -15.35946                           |
| 4                                    | -0.92918                           | 0                                  | 0                                  | 0                                  | 0                                  | 0.86359                     | -15.75493                                         | -15.56407                           |
| 5                                    | -0.54343                           | -0.54343                           | 0                                  | 0                                  | 0                                  | 0.85503                     | -15.91261                                         | -15.72175                           |
| 6                                    | -1.13379                           | 0                                  | 0                                  | 0                                  | 0                                  | 0.85252                     | -15.95954                                         | -15.76868                           |
| 7                                    | -0.60631                           | -0.60631                           | 0                                  | 0                                  | 0                                  | 0.84833                     | -16.03838                                         | -15.84752                           |
| 8                                    | -0.46459                           | -0.92918                           | 0                                  | 0                                  | 0                                  | 0.83885                     | -16.21953                                         | -16.02866                           |
| 9                                    | -0.72457                           | -0.72457                           | 0                                  | 0                                  | 0                                  | 0.83600                     | -16.27490                                         | -16.08404                           |
| 10                                   | -0.92918                           | -0.60631                           | 0                                  | 0                                  | 0                                  | 0.83159                     | -16.36125                                         | -16.17038                           |
| 11                                   | -0.92918                           | -0.72457                           | 0                                  | 0                                  | 0                                  | 0.82562                     | -16.47951                                         | -16.28864                           |
| 12                                   | -0.85035                           | -0.85035                           | 0                                  | 0                                  | 0                                  | 0.82327                     | -16.52644                                         | -16.33558                           |
| 13                                   | -0.92918                           | -0.92918                           | 0                                  | 0                                  | 0                                  | 0.81549                     | -16.68411                                         | -16.49325                           |
| 14                                   | -1.13379                           | -0.72457                           | 0                                  | 0                                  | 0                                  | 0.81549                     | -16.68412                                         | -16.49325                           |
| 15                                   | -1.13379                           | -0.92918                           | 0                                  | 0                                  | 0                                  | 0.80561                     | -16.88873                                         | -16.69786                           |
| 16                                   | -0.85035                           | -0.85035                           | -0.46459                           | 0                                  | 0                                  | 0.80076                     | -16.99103                                         | -16.80017                           |
| 17                                   | -0.85034                           | -0.85034                           | -0.56690                           | 0                                  | 0                                  | 0.79597                     | -17.09334                                         | -16.90247                           |
| 18                                   | -1.13379                           | -1.13380                           | 0                                  | 0                                  | 0                                  | 0.79597                     | -17.09334                                         | -16.90248                           |
| 19                                   | -0.85035                           | -0.54343                           | 0.00000                            | -0.92918                           | 0                                  | 0.79340                     | -17.14871                                         | -16.95785                           |
| 20                                   | -0.85035                           | -0.56690                           | -0.92918                           | 0                                  | 0                                  | 0.79232                     | -17.17218                                         | -16.98132                           |
| 21                                   | -0.54343                           | -0.54343                           | -0.56690                           | -0.92918                           | 0                                  | 0.78155                     | -17.40869                                         | -17.21783                           |
| 22                                   | -0.85034                           | -0.28345                           | -0.54343                           | -0.92918                           | 0                                  | 0.78050                     | -17.43216                                         | -17.24130                           |
| 23                                   | -0.92918                           | -0.92918                           | -0.92918                           | 0                                  | 0                                  | 0.77247                     | -17.61330                                         | -17.42243                           |
| 24                                   | -0.85034                           | -0.54343                           | -0.56690                           | -0.92918                           | 0                                  | 0.76801                     | -17.71560                                         | -17.52474                           |
| 25                                   | -0.85034                           | -0.54343                           | -0.60631                           | -0.92918                           | 0                                  | 0.76631                     | -17.75502                                         | -17.56416                           |
| 26                                   | -1.13379                           | -0.92918                           | -0.92918                           | 0                                  | 0                                  | 0.76360                     | -17.81791                                         | -17.62704                           |

|    |          |          |          |          |   |         |           |           |
|----|----------|----------|----------|----------|---|---------|-----------|-----------|
| 27 | -1.13379 | -1.13380 | -0.72457 | 0        | 0 | 0.76360 | -17.81791 | -17.62705 |
| 28 | -0.46459 | -0.85035 | -0.85035 | -0.92918 | 0 | 0.75924 | -17.92022 | -17.72935 |
| 29 | -1.13380 | -1.13379 | -0.92918 | 0        | 0 | 0.75493 | -18.02252 | -17.83166 |
| 30 | -1.13379 | -1.13379 | -1.13379 | 0        | 0 | 0.74646 | -18.22713 | -18.03627 |

The energy of the MO is matched to each of the participating outermost atomic or hybridized orbitals of the bonding atoms wherein the energy match includes the energy contribution due to the AO or HO's donation of charge to the MO. The force constant  $k'$  (Eq. (15.1)) is used to determine the ellipsoidal parameter  $c'$  (Eq. (15.2)) of the each  $H_2$ -type-ellipsoidal-MO in terms of the central force of the foci. Then,  $c'$  is substituted into the energy equation (from Eq. (15.11))) which is set equal to  $n_1$  times the total energy of  $H_2$  where  $n_1$  is the number of equivalent bonds of the MO and the energy of  $H_2$ ,  $-31.63536831 \text{ eV}$ , Eq. (11.212) is the minimum energy possible for a prolate spheroidal MO. From the energy equation and the relationship between the axes, the dimensions of the MO are solved. The energy equation has the semimajor axis  $a$  as its only parameter. The solution of the semimajor axis  $a$  then allows for the solution of the other axes of each prolate spheroid and eccentricity of each MO (Eqs. (15.3-15.5)). The parameter solutions then allow for the component and total energies of the MO to be determined.

The total energy,  $E_T(H_2MO)$ , is given by the sum of the energy terms (Eqs. (15.6-15.11)) plus  $E_T(AO/HO)$ :

$$E_T(H_2MO) = V_e + T + V_m + V_p + E_T(AO/HO) \quad (15.36)$$

$$\begin{aligned} E_T(H_2MO) &= -\frac{n_1 e^2}{8\pi\epsilon_0 \sqrt{a^2 - b^2}} \left[ c_1 c_2 \left( 2 - \frac{a_0}{a} \right) \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} - 1 \right] + E_T(AO/HO) \\ &= -\frac{n_1 e^2}{8\pi\epsilon_0 c'} \left[ c_1 c_2 \left( 2 - \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] + E_T(AO/HO) \end{aligned} \quad (15.37)$$

where  $n_1$  is the number of equivalent bonds of the MO,  $c_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the group,  $c_2$  is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of each chemical bond, and  $E_T(AO/HO)$  is the total energy comprising the difference of the energy  $E(AO/HO)$  of at least one atomic or hybrid orbital to which the MO is energy matched and any energy component  $\Delta E_{H_2MO}(AO/HO)$  due to the AO or HO's charge donation to the MO.

$$E_T(AO/HO) = E(AO/HO) - \Delta E_{H_2MO}(AO/HO) \quad (15.38)$$

As specific examples given in previous sections,  $E_T(AO / HO)$  is one from the group of

$$E_T(AO / HO) = E(O2p \text{ shell}) = -E(\text{ionization}; O) = -13.6181 \text{ eV};$$

$$E_T(AO / HO) = E(N2p \text{ shell}) = -E(\text{ionization}; N) = -14.53414 \text{ eV};$$

$$E_T(AO / HO) = E(C, 2sp^3) = -14.63489 \text{ eV};$$

$$5 \quad E_T(AO / HO) = E_{Coulomb}(Cl, 3sp^3) = -14.60295 \text{ eV};$$

$$E_T(AO / HO) = E(\text{ionization}; C) + E(\text{ionization}; C^+);$$

$$E_T(AO / HO) = E(C_{ethane}, 2sp^3) = -15.35946 \text{ eV};$$

$$E_T(AO / HO) = +E(C_{ethylene}, 2sp^3) - E(C_{ethylene}, 2sp^3);$$

$$E_T(AO / HO) = E(C, 2sp^3) - 2E_T(C = C, 2sp^3) = -14.63489 \text{ eV} - (-2.26758 \text{ eV});$$

$$10 \quad E_T(AO / HO) = E(C_{acetylene}, 2sp^3) - E(C_{acetylene}, 2sp^3) - E(C_{acetylene}, 2sp^3) = 16.20002 \text{ eV};$$

$$E_T(AO / HO) = E(C, 2sp^3) - 2E_T(C \equiv C, 2sp^3) = -14.63489 \text{ eV} - (-3.13026 \text{ eV});$$

$$E_T(AO / HO) = E(C_{benzene}, 2sp^3) - E(C_{benzene}, 2sp^3);$$

$$E_T(AO / HO) = E(C, 2sp^3) - E_T(C = C, 2sp^3) = -14.63489 \text{ eV} - (-1.13379 \text{ eV}), \text{ and}$$

$$E_T(AO / HO) = E(C_{alkane}, 2sp^3) = -15.56407 \text{ eV}.$$

$$15 \quad \text{To solve the bond parameters and energies, } c' = a \sqrt{\frac{\hbar^2 4\pi\epsilon_0}{m_e e^2 2C_1 C_2 a}} = \sqrt{\frac{aa_0}{2C_1 C_2}} \quad (\text{Eq.}$$

(15.2)) is substituted into  $E_T(H_2MO)$  to give

$$\begin{aligned} E_T(H_2MO) &= -\frac{n_1 e^2}{8\pi\epsilon_0 \sqrt{a^2 - b^2}} \left[ c_1 c_2 \left( 2 - \frac{a_0}{a} \right) \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}} - 1 \right] + E_T(AO / HO) \\ &= -\frac{n_1 e^2}{8\pi\epsilon_0 c'} \left[ c_1 c_2 \left( 2 - \frac{a_0}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] + E_T(AO / HO) \\ &= -\frac{n_1 e^2}{8\pi\epsilon_0 \sqrt{\frac{aa_0}{2C_1 C_2}}} \left[ c_1 c_2 \left( 2 - \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2C_1 C_2}}}{a - \sqrt{\frac{aa_0}{2C_1 C_2}}} - 1 \right] + E_T(AO / HO) \end{aligned} \quad (15.39)$$

The total energy is set equal to  $E(\text{basis energies})$  which in the most general case is given by



the sum of a first integer  $n_1$  times the total energy of  $H_2$  minus a second integer  $n_2$  times the total energy of  $H$ , minus a third integer  $n_3$  times the valence energy of  $E(AO)$  (e.g.  $E(N) = -14.53414 \text{ eV}$ ) where the first integer can be 1, 2, 3..., and each of the second and third integers can be 0, 1, 2, 3....

$$5 \quad E(\text{basis energies}) = n_1(-31.63536831 \text{ eV}) - n_2(-13.605804 \text{ eV}) - n_3 E(AO) \quad (15.40)$$

In the case that the MO bonds two atoms other than hydrogen,  $E(\text{basis energies})$  is  $n_1$  times the total energy of  $H_2$  where  $n_1$  is the number of equivalent bonds of the MO and the energy of  $H_2$ ,  $-31.63536831 \text{ eV}$ , Eq. (11.212) is the minimum energy possible for a prolate spheroidal MO:

$$10 \quad E(\text{basis energies}) = n_1(-31.63536831 \text{ eV}) \quad (15.41)$$

$E_T(H_2MO)$ , is set equal to  $E(\text{basis energies})$ , and the semimajor axis  $a$  is solved.

Thus, the semimajor axis  $a$  is solved from the equation of the form:

$$-\frac{n_1 e^2}{8\pi\epsilon_0 \sqrt{\frac{aa_0}{2C_1 C_2}}} \left[ c_1 c_2 \left( 2 - \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2C_1 C_2}}}{a - \sqrt{\frac{aa_0}{2C_1 C_2}}} - 1 \right] + E_T(AO / HO) = E(\text{basis energies}) \quad (15.42)$$

The distance from the origin of the  $H_2$ -type-ellipsoidal-MO to each focus  $c'$ , the internuclear distance  $2c'$ , and the length of the semiminor axis of the prolate spheroidal  $H_2$ -type MO  $b = c$  are solved from the semimajor axis  $a$  using Eqs. (15.2-15.4). Then, the component energies are given by Eqs. (15.6-15.9) and (15.39).

The total energy of the MO of the functional group,  $E_T(MO)$ , is the sum of the total energy of the components comprising the energy contribution of the MO formed between the participating atoms and  $E_T(\text{atom} - \text{atom}, msp^3.AO)$ , the change in the energy of the AOs or HOs upon forming the bond. From Eqs. (15.39-15.40),  $E_T(MO)$  is

$$E_T(MO) = E(\text{basis energies}) + E_T(\text{atom} - \text{atom}, msp^3.AO) \quad (15.43)$$

During bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy  $\bar{E}_{osc}$  is the sum of the Doppler,  $\bar{E}_D$ , and average vibrational kinetic energies,  $\bar{E}_{Kvib}$ :

$$\bar{E}_{osc} = n_1 (\bar{E}_D + \bar{E}_{Kvib}) = n_1 \left( E_{hv} \sqrt{\frac{2\bar{E}_K}{m_e c^2}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \quad (15.44)$$

where  $n_1$  is the number of equivalent bonds of the MO,  $k$  is the spring constant of the equivalent harmonic oscillator, and  $\mu$  is the reduced mass. The angular frequency of the reentrant oscillation in the transition state corresponding to  $\bar{E}_D$  is determined by the force  
5 between the central field and the electrons in the transition state. The force and its derivative are given by

$$f(R) = -c_{BO} \frac{C_{1o} C_{2o} e^2}{4\pi\epsilon_0 R^3} \quad (15.45)$$

and

$$f'(a) = 2c_{BO} \frac{C_{1o} C_{2o} e^2}{4\pi\epsilon_0 R^3} \quad (15.46)$$

10 such that the angular frequency of the oscillation in the transition state is given by

$$\omega = \sqrt{\frac{\left[ \frac{-3}{a} f(a) - f'(a) \right]}{m_e}} = \sqrt{\frac{k}{m_e}} = \sqrt{\frac{c_{BO} \frac{C_{1o} C_{2o} e^2}{4\pi\epsilon_0 R^3}}{m_e}} \quad (15.47)$$

where  $R$  is the semimajor axis  $a$  or the semiminor axis  $b$  depending on the eccentricity of the bond that is most representative of the oscillation in the transition state,  $c_{BO}$  is the bond-order factor which is 1 for a single bond and when the MO comprises  $n_1$  equivalent single  
15 bonds as in the case of functional groups.  $c_{BO}$  is 4 for an independent double bond as in the case of the  $CO_2$  and  $NO_2$  molecules and 9 for an independent triplet bond.  $C_{1o}$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of the oscillatory transition state of a chemical bond of the group, and  $C_{2o}$  is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the transition state of the chemical bond.  
20 Typically,  $C_{1o} = C_1$  and  $C_{2o} = C_2$ . The kinetic energy,  $E_K$ , corresponding to  $\bar{E}_D$  is given by Planck's equation for functional groups:

$$\bar{E}_K = \hbar\omega = \hbar \sqrt{\frac{C_{1o} C_{2o} e^2}{4\pi\epsilon_0 R^3 m_e}} \quad (15.48)$$

The Doppler energy of the electrons of the reentrant orbit is

467

$$\bar{E}_D \cong E_{hv} \sqrt{\frac{2\bar{E}_K}{m_e c^2}} = E_{hv} \sqrt{\frac{2\hbar \sqrt{\frac{C_{1o} C_{2o} e^2}{4\pi\epsilon_0 R^3}}}{m_e c^2}} \quad (15.49)$$

$\bar{E}_{osc}$  given by the sum of  $\bar{E}_D$  and  $\bar{E}_{Kvib}$  is

$$\bar{E}_{osc} (group) = n_1 (\bar{E}_D + \bar{E}_{Kvib}) = n_1 \left( E_{hv} \sqrt{\frac{2\hbar \sqrt{\frac{C_{1o} C_{2o} e^2}{4\pi\epsilon_0 R^3}}}{m_e c^2}} + E_{vib} \right) \quad (15.50)$$

$E_{hv}$  of a group having  $n_1$  bonds is given by  $E_T (MO) / n_1$  such that

$$5 \quad \bar{E}_{osc} = n_1 (\bar{E}_D + \bar{E}_{Kvib}) = n_1 \left( E_T (MO) / n_1 \sqrt{\frac{2\bar{E}_K}{Mc^2}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right) \quad (15.51)$$

$E_{T+osc} (Group)$  is given by the sum of  $E_T (MO)$  (Eq. (15.42)) and  $\bar{E}_{osc}$  (Eq. (15.51)):

$$\begin{aligned} E_{T+osc} (Group) &= E_T (MO) + \bar{E}_{osc} \\ &= \left( \left[ -\frac{n_1 e^2}{8\pi\epsilon_0 \sqrt{\frac{aa_0}{2C_1 C_2}}} \left[ c_1 c_2 \left( 2 - \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2C_1 C_2}}}{a - \sqrt{\frac{aa_0}{2C_1 C_2}}} - 1 \right] \right] \right. \\ &\quad \left. + E_T (AO / HO) + E_T (atom - atom, msp^3 . AO) \right) \\ &\quad \left[ 1 + \sqrt{\frac{2\hbar \sqrt{\frac{C_{1o} C_{2o} e^2}{4\pi\epsilon_0 R^3}}}{m_e c^2}} \right] + n_1 \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \\ &= \left( E(basis \text{ energies}) + E_T (atom - atom, msp^3 . AO) \right) \left[ 1 + \sqrt{\frac{2\hbar \sqrt{\frac{C_{1o} C_{2o} e^2}{4\pi\epsilon_0 R^3}}}{m_e c^2}} \right] + n_1 \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \end{aligned} \quad (15.52)$$

The total energy of the functional group  $E_T(\text{group})$  is the sum of the total energy of the components comprising the energy contribution of the MO formed between the participating atoms,  $E(\text{basis energies})$ , the change in the energy of the AOs or HOs upon forming the bond ( $E_T(\text{atom} - \text{atom}, msp^3.AO)$ ), the energy of oscillation in the transition state, and the  
 5 change in magnetic energy with bond formation,  $E_{mag}$ . From Eq. (15.52), the total energy of the group  $E_T(\text{Group})$  is

$$E_T(\text{Group}) = \left( \left( E(\text{basis energies}) + E_T(\text{atom} - \text{atom}, msp^3.AO) \right) \left[ 1 + \sqrt{\frac{2\hbar \sqrt{\frac{C_{1o} C_{2o} e^2}{4\pi\epsilon_o R^3}}}{m_e c^2}} \right] \right) + n_1 \bar{E}_{Kvib} + E_{mag} \quad (15.53)$$

The change in magnetic energy  $E_{mag}$  which arises due to the formation of unpaired electrons in the corresponding fragments relative to the bonded group is given by

$$10 \quad E_{mag} = c_3 \frac{2\pi\mu_o e^2 \hbar^2}{m_e^2 r^3} = c_3 \frac{8\pi\mu_o \mu_B^2}{r^3} \quad (15.54)$$

where  $r^3$  is the radius of the atom that reacts to form the bond and  $c_3$  is the number of electron pairs.

$$E_T(\text{Group}) = \left( \left( E(\text{basis energies}) + E_T(\text{atom} - \text{atom}, msp^3.AO) \right) \left[ 1 + \sqrt{\frac{2\hbar \sqrt{\frac{C_{1o} C_{2o} e^2}{4\pi\epsilon_o R^3}}}{m_e c^2}} \right] \right) + n_1 \bar{E}_{Kvib} + c_3 \frac{8\pi\mu_o \mu_B^2}{r^3} \quad (15.55)$$

The total bond energy of the group  $E_D(\text{Group})$  is the negative difference of the total energy of  
 15 the group (Eq. (15.55)) and the total energy of the starting species given by the sum of  $c_4 E_{initial}(c_4 AO / HO)$  and  $c_5 E_{initial}(c_5 AO / HO)$ :

$$E_D (Group) = - \left( E(basis\ energies) + E_T (atom - atom, msp^3 . AO) \right) \left[ 1 + \sqrt{\frac{C_{1o} C_{2o} e^2}{4\pi\epsilon_o R^3} \frac{2\hbar}{m_e c^2}} \right] + n_1 \bar{E}_{Kvib} + c_3 \frac{8\pi\mu_o \mu_B^2}{r_n^3} - (c_4 E_{initial} (AO / HO) + c_5 E_{initial} (c_5 AO / HO)) \quad (15.56)$$

In the case of organic molecules, the atoms of the functional groups are energy matched to the  $C2sp^3$  HO such that

$$E(AO / HO) = -14.63489\ eV \quad (15.57)$$

5 For examples of  $E_{mag}$  from previous sections:

$$E_{mag} (C2sp^3) = c_3 \frac{8\pi\mu_o \mu_B^2}{r^3} = c_3 \frac{8\pi\mu_o \mu_B^2}{(0.91771a_0)^3} = c_3 0.14803\ eV \quad (15.58)$$

$$E_{mag} (O2p) = c_3 \frac{8\pi\mu_o \mu_B^2}{r^3} = c_3 \frac{8\pi\mu_o \mu_B^2}{a_0^3} = c_3 0.11441\ eV \quad (15.59)$$

$$E_{mag} (N2p) = c_3 \frac{8\pi\mu_o \mu_B^2}{r^3} = c_3 \frac{8\pi\mu_o \mu_B^2}{(0.93084a_0)^3} = c_3 0.14185\ eV \quad (15.60)$$

In the general case of the solution of an organic functional group, the geometric bond parameters are solved from the semimajor axis and the relationships between the parameters by first using Eq. (15.42) to arrive at  $a$ . Then, the remaining parameters are determined using Eqs. (15.1-15.5). Next, the energies are given by Eqs. (15.52-15.59). To meet the equipotential condition for the union of the  $H_2$ -type-ellipsoidal-MO and the HO or AO of the atom of a functional group, the factor  $c_2$  of a  $H_2$ -type ellipsoidal MO in principal Eqs. (15.42) and (15.52) may given by

(i) one:

$$c_2 = 1 \quad (15.61)$$

(ii) the ratio that is less than one of  $13.605804\ eV$ , the magnitude of the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243), and the magnitude of the

Coulombic energy of the participating AO or HO of the atom,  $E_{Coulomb}(MO.atom,msp^3)$  given by Eqs. (15.19) and (15.31-15.32). For  $|E_{Coulomb}(MO.atom,msp^3)| > 13.605804 \text{ eV}$  :

$$c_2 = \frac{\frac{e^2}{8\pi\epsilon_0 a_0}}{\frac{e^2}{8\pi\epsilon_0 r_{A-B \text{ AorBsp}^3}}} = \frac{13.605804 \text{ eV}}{|E_{Coulomb}(MO.atom,msp^3)|} \quad (15.62)$$

For  $|E_{Coulomb}(MO.atom,msp^3)| < 13.605804 \text{ eV}$  :

$$c_2 = \frac{\frac{e^2}{8\pi\epsilon_0 r_{A-B \text{ AorBsp}^3}}}{\frac{e^2}{8\pi\epsilon_0 a_0}} = \frac{|E_{Coulomb}(MO.atom,msp^3)|}{13.605804 \text{ eV}} \quad (15.63)$$

(iii) the ratio that is less than one of 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243), and the magnitude of the valence energy,  $E(valence)$ , of the participating AO or HO of the atom where  $E(valence)$  is the ionization energy or  $E(MO.atom,msp^3)$  given by Eqs. (15.20) and (15.31-15.32). For  $|E(valence)| > 13.605804 \text{ eV}$  :

$$c_2 = \frac{\frac{e^2}{8\pi\epsilon_0 a_0}}{\frac{e^2}{8\pi\epsilon_0 r_{A-B \text{ AorBsp}^3}}} = \frac{13.605804 \text{ eV}}{|E(valence)|} \quad (15.64)$$

For  $|E(valence)| < 13.605804 \text{ eV}$  :

$$c_2 = \frac{\frac{e^2}{8\pi\epsilon_0 r_{A-B \text{ AorBsp}^3}}}{\frac{e^2}{8\pi\epsilon_0 a_0}} = \frac{|E(valence)|}{13.605804 \text{ eV}} \quad (15.65)$$

15

(iv) the ratio that is less than one of the magnitude of the Coulombic energy of the participating AO or HO of a first atom,  $E_{Coulomb}(MO.atom,msp^3)$  given by Eqs. (15.19) and (15.31-15.32), and the magnitude of the valence energy,  $E(valence)$ , of the participating AO or HO of a second atom to which the first is energy matched where  $E(valence)$  is the

ionization energy or  $E(MO.atom,msp^3)$  given by Eqs. (15.20) and (15.31-15.32). For

$$|E_{Coulomb}(MO.atom,msp^3)| > E(valence):$$

$$c_2 = \frac{|E(valence)|}{|E_{Coulomb}(MO.atom,msp^3)|} \quad (15.66)$$

$$\text{For } |E_{Coulomb}(MO.atom,msp^3)| < E(valence):$$

$$c_2 = \frac{|E_{Coulomb}(MO.atom,msp^3)|}{|E(valence)|} \quad (15.67)$$

(v) the ratio that is less than one of the magnitude of the valence-level energies,  $E_n(valence)$ , of the AO or HO of the nth participating atom of two that are energy matched where  $E(valence)$  is the ionization energy or  $E(MO.atom,msp^3)$  given by Eqs. (15.20) and (15.31-15.32):

$$c_2 = \frac{E_1(valence)}{E_2(valence)} \quad (15.68)$$

(vi) the factor that is the ratio of the hybridization factor  $c_2(1)$  of the valence AO or HO of a first atom and the hybridization factor  $c_2(2)$  of the valence AO or HO of a second atom to which the first is energy matched where  $c_2(n)$  is given by Eqs. (15.62-15.68); alternatively  $c_2$  is the hybridization factor  $c_2(1)$  of the valence AOs or HOs a first pair of atoms and the hybridization factor  $c_2(2)$  of the valence AO or HO a third atom or second pair to which the first two are energy matched:

$$c_2 = \frac{c_2(1)}{c_2(2)} \quad (15.69)$$

(vii) the factor that is the product of the hybridization factor  $c_2(1)$  of the valence AO or HO of a first atom and the hybridization factor  $c_2(2)$  of the valence AO or HO of a second atom to which the first is energy matched where  $c_2(n)$  is given by Eqs. (15.62-15.69);

alternatively  $c_2$  is the hybridization factor  $c_2(1)$  of the valence AOs or HOs a first pair of atoms and the hybridization factor  $c_2(2)$  of the valence AO or HO a third atom or second pair to which the first two are energy matched:

$$c_2 = c_2(1)c_2(2) \quad (15.70)$$

- 5 The hybridization factor  $c_2$  corresponds to the force constant  $k$  (Eqs. (11.65) and (13.58)). In the case that the valence or Coulombic energy of the AO or HO is less than 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243), then  $C_2$  corresponding to  $k'$  (Eq. (15.1)) is given by Eqs. (15.62-15.70).

Specific examples of the factors  $c_2$  and  $C_2$  of a  $H_2$ -type ellipsoidal MO of Eq. 10 (15.51) given in following sections are

$$\begin{aligned} c_2(C2sp^3HO \text{ to } F) &= \frac{E(C, 2sp^3)}{E(F)} c_2(C2sp^3HO) = \frac{-14.63489 \text{ eV}}{-17.42282 \text{ eV}} (0.91771) = 0.77087; \\ C_2(C2sp^3HO \text{ to } Cl) &= \frac{E(Cl)}{E(C, 2sp^3)} c_2(C2sp^3HO) = \frac{-12.96764 \text{ eV}}{-14.63489 \text{ eV}} (0.91771) = 0.81317; \\ C_2(C2sp^3HO \text{ to } Br) &= \frac{E(Br)}{E(C, 2sp^3)} c_2(C2sp^3HO) = \frac{-11.81381 \text{ eV}}{-14.63489 \text{ eV}} (0.91771) = 0.74081; \\ C_2(C2sp^3HO \text{ to } I) &= \frac{E(I)}{E(C, 2sp^3)} c_2(C2sp^3HO) = \frac{-10.45126 \text{ eV}}{-14.63489 \text{ eV}} (0.91771) = 0.65537; \\ 15 \quad c_2(C2sp^3HO \text{ to } O) &= \frac{E(O)}{E(C, 2sp^3)} c_2(C2sp^3HO) = \frac{-13.61806 \text{ eV}}{-14.63489 \text{ eV}} (0.91771) = 0.85395; \\ c_2(H \text{ to } 1^\circ N) &= \frac{E(N)}{E(C, 2sp^3)} = \frac{-14.53414 \text{ eV}}{-15.35946 \text{ eV}} = 0.94627; \\ c_2(C2sp^3HO \text{ to } N) &= \frac{E(N)}{E(C, 2sp^3)} c_2(C2sp^3HO) = \frac{-14.53414 \text{ eV}}{-14.63489 \text{ eV}} (0.91771) = 0.91140; \\ c_2(H \text{ to } 2^\circ N) &= \frac{E(N)}{E(C, 2sp^3)} = \frac{-14.53414 \text{ eV}}{-15.56407 \text{ eV}} = 0.93383; \\ C_2(S3p \text{ to } H) &= \frac{E(S, 3p)}{E(H)} = \frac{-10.36001 \text{ eV}}{-13.60580 \text{ eV}} = 0.76144; \\ 20 \quad C_2(C2sp^3HO \text{ to } S) &= \frac{E(S)}{E(C, 2sp^3)} c_2(C2sp^3HO) = \frac{-10.36001 \text{ eV}}{-14.63489 \text{ eV}} (0.91771) = 0.64965; \end{aligned}$$



473

$$\begin{aligned}
 c_2(O \text{ to } S3sp^3 \text{ to } C2sp^3HO) &= \frac{E(O)}{E(S)} c_2(C2sp^3HO) \\
 &= \frac{-13.61806 \text{ eV}}{-10.36001 \text{ eV}} (0.91771); \\
 &= 1.20632
 \end{aligned}$$

$$c_2(S3sp^3) = \frac{E_{Coulomb}(S3sp^3)}{E(H)} = \frac{-11.57099 \text{ eV}}{-13.60580 \text{ eV}} = 0.85045;$$

$$C_2(C2sp^3HO \text{ to } S3sp^3) = \frac{E(S3sp^3)}{E(C, 2sp^3)} c_2(S3sp^3) = \frac{-11.52126 \text{ eV}}{-14.63489 \text{ eV}} (0.85045) = 0.66951;$$

$$\begin{aligned}
 C_2(S3sp^3 \text{ to } O \text{ to } C2sp^3HO) &= \frac{E(S, 3sp^3)}{E(O, 2p)} c_2(C2sp^3HO) \\
 &= \frac{-11.52126 \text{ eV}}{-13.61806 \text{ eV}} (0.91771); \\
 &= 0.77641
 \end{aligned}$$

$$\begin{aligned}
 c_2(O \text{ to } N2p \text{ to } C2sp^3HO) &= \frac{E(O)}{E(N)} c_2(C2sp^3HO) \\
 &= \frac{-13.61806 \text{ eV}}{-14.53414 \text{ eV}} (0.91771); \\
 &= 0.85987
 \end{aligned}$$

5

$$c_2(N2p \text{ to } O2p) = \frac{c_2(C2sp^3HO \text{ to } N)}{c_2(C2sp^3HO \text{ to } O)} = \frac{0.91140}{0.85395} = 1.06727;$$

$$C_2(\text{benzene}C2sp^3HO) = c_2(\text{benzene}C2sp^3HO) = \frac{13.605804 \text{ eV}}{15.95955 \text{ eV}} = 0.85252;$$

$$\begin{aligned}
 c_2(\text{aryl}C2sp^3HO \text{ to } O) &= \frac{E(O)}{E(C, 2sp^3)} c_2(\text{aryl}C2sp^3HO) \\
 &= \frac{-13.61806 \text{ eV}}{-14.63489 \text{ eV}} (0.85252) \quad ; \\
 &= 0.79329
 \end{aligned}$$

$$c_2(H \text{ to aniline } N) = \frac{E(N)}{E(C, 2sp^3)} = \frac{-14.53414 \text{ eV}}{-15.76868 \text{ eV}} = 0.92171;$$

$$\begin{aligned}
 c_2(\text{aryl}C2sp^3HO \text{ to } N) &= \frac{E(N)}{E(C, 2sp^3)} c_2(\text{aryl}C2sp^3HO) \\
 &= \frac{-14.53414 \text{ eV}}{-14.63489 \text{ eV}} (0.85252) \quad , \\
 &= 0.84665
 \end{aligned}$$

10

and

$$C_2 \left( S3p \text{ to aryl-type } C2sp^3 HO \right) = \frac{E(S, 3p)}{E(C, 2sp^3)} = \frac{-10.36001 \text{ eV}}{-15.76868 \text{ eV}} = 0.65700.$$

## MO INTERCEPT ANGLES AND DISTANCES

Consider the general case of Eqs. (13.84-13.95) wherein the nucleus of a  $B$  atom and the nucleus of a  $A$  atom comprise the foci of each  $H_2$ -type ellipsoidal MO of an  $A-B$  bond.

The parameters of the point of intersection of each  $H_2$ -type ellipsoidal MO and the  $A$ -atom AO are determined from the polar equation of the ellipse:

$$r = r_0 \frac{1+e}{1+e \cos \theta'} \quad (15.71)$$

The radius of the  $A$  shell is  $r_A$ , and the polar radial coordinate of the ellipse and the radius of the  $A$  shell are equal at the point of intersection such that

$$r_A = (a - c') \frac{1 + \frac{c'}{a}}{1 + \frac{c'}{a} \cos \theta'} \quad (15.72)$$

The polar angle  $\theta'$  at the intersection point is given by

$$\theta' = \cos^{-1} \left( \frac{a}{c'} \left( (a - c') \frac{1 + \frac{c'}{a}}{a_0} - 1 \right) \right) \quad (15.73)$$

Then, the angle  $\theta_{AAO}$  the radial vector of the  $A$  AO makes with the internuclear axis is

$$\theta_{AAO} = 180^\circ - \theta' \quad (15.74)$$

The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals such that the angle  $\omega t = \theta_{H_2MO}$  between the internuclear axis and the point of intersection of each  $H_2$ -type ellipsoidal MO with the  $A$  radial vector obeys the following relationship:

$$r_A \sin \theta_{AAO} = b \sin \theta_{H_2MO} \quad (15.75)$$

such that

$$\theta_{H_2MO} = \sin^{-1} \frac{r_A \sin \theta_{AAO}}{b} \quad (15.76)$$

The distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H_2MO} = a \cos \theta_{H_2MO} \quad (15.77)$$

The distance  $d_{AAO}$  along the internuclear axis from the origin of the  $A$  atom to the point of intersection of the orbitals is given by

$$d_{AAO} = c' - d_{H_2MO} \quad (15.78)$$

## BOND ANGLES

Further consider an  $ACB$  MO comprising a linear combination of  $C-A$ -bond and  $C-B$ -bond MOs where  $C$  is the general central atom. A bond is also possible between the  $A$  and  $B$  atoms of the  $C-A$  and  $C-B$  bonds. Such  $A-B$  bonding would decrease the  $C-A$  and  $C-B$  bond strengths since electron density would be shifted from the latter bonds to the former bond. Thus, the  $\angle ACB$  bond angle is determined by the condition that the total energy of the  $H_2$ -type ellipsoidal MO between the terminal  $A$  and  $B$  atoms is zero. The force constant  $k'$  of a  $H_2$ -type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by:

$$k' = \frac{C_1 C_2 2e^2}{4\pi\epsilon_0} \quad (15.79)$$

where  $C_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the molecule which is 0.75 (Eq. (13.59)) for a terminal  $A-H$  ( $A$  is  $H$  or other atom) and 1 otherwise and  $C_2$  is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the chemical bond and is equal to the corresponding factor of Eqs. (15.42) and (15.52). The distance from the origin of the MO to each focus  $c'$  of the  $A-B$  ellipsoidal MO is given by:

$$c' = a \sqrt{\frac{\hbar^2 4\pi\epsilon_0}{m_e e^2 2C_1 C_2 a}} = \sqrt{\frac{aa_0}{2C_1 C_2}} \quad (15.80)$$

The internuclear distance is

$$2c' = 2 \sqrt{\frac{aa_0}{2C_1 C_2}} \quad (15.81)$$

The length of the semiminor axis of the prolate spheroidal  $A-B$  MO  $b=c$  is given by Eq. (15.4).

The component energies and the total energy,  $E_T(H_2MO)$ , of the  $A-B$  bond are given by the energy equations (Eqs. (11.207-11.212), (11.213-11.217), and (11.239)) of  $H_2$  except that the terms based on charge are multiplied by  $c_{BO}$ , the bond-order factor which is 1 for a single bond and when the MO comprises  $n_1$  equivalent single bonds as in the case of functional groups.  $c_{BO}$  is 4 for an independent double bond as in the case of the  $CO_2$  and  $NO_2$  molecules. The kinetic energy term is multiplied by  $c'_{BO}$  which is 1 for a single bond, 2 for a double bond, and 9/2 for a triple bond. The electron energy terms are multiplied by  $c_1$ , the fraction of the  $H_2$ -type ellipsoidal MO basis function of a terminal chemical bond which is 0.75 (Eq. (13.233)) for a terminal  $A-H$  ( $A$  is  $H$  or other atom) and 1 otherwise. The electron energy terms are further multiplied by  $c'_2$ , the hybridization or energy-matching factor that results in an equipotential energy match of the participating at least two atomic orbitals of each terminal bond. Furthermore, when  $A-B$  comprises atoms other than  $H$ ,  $E_T(atom - atom, msp^3.AO)$ , the energy component due to the AO or HO's charge donation to the terminal MO, is added to the other energy terms to give  $E_T(H_2MO)$ :

$$E_T(H_2MO) = \frac{-e^2}{8\pi\epsilon_0 c'} \left[ c_1 c'_2 \left( 2c_{BO} - c'_{BO} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] + E_T(atom - atom, msp^3.AO) \quad (15.82)$$

The radiation reaction force in the case of the vibration of  $A-B$  in the transition state corresponds to the Doppler energy,  $E_D$ , given by Eq. (11.181) that is dependent on the motion of the electrons and the nuclei. The total energy that includes the radiation reaction of the  $A-B$  MO is given by the sum of  $E_T(H_2MO)$  (Eq. (15.82)) and  $\bar{E}_{osc}$  given Eqs. (11.213-11.220), (11.231-11.236), and (11.239-11.240). Thus, the total energy  $E_T(A-B)$  of the  $A-B$  MO including the Doppler term is

$$E_T(A-B) = \left[ \left( \frac{-e^2}{8\pi\epsilon_0 c'} \left[ c_1 c_2' \left( 2c_{BO} - c'_{BO} \frac{a_0}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] + E_T(\text{atom} - \text{atom}, msp^3, AO) \right) \right] \quad (15.83)$$

$$\left[ 1 + \sqrt{\frac{2\hbar \sqrt{\frac{c_{BO} C_{10} C_{20} e^2}{4\pi\epsilon_0 a^3}}}{m_e c^2}} + \frac{1}{2} \sqrt{\frac{c_{BO} \frac{c_1 c_2' e^2}{8\pi\epsilon_0 a^3} - \frac{c_{BO} e^2}{8\pi\epsilon_0 (a+c')^3}}{\mu}} \right]$$

where  $C_{10}$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of the oscillatory transition state of the  $A-B$  bond which is 0.75 (Eq. (13.233)) in the case of  $H$  bonding to a central atom and 1 otherwise,  $C_{20}$  is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the transition state of the chemical bond, and  $\mu = \frac{m_1 m_2}{m_1 + m_2}$  is the reduced mass of the nuclei given by Eq. (11.154). To match the boundary condition that the total energy of the  $A-B$  ellipsoidal MO is zero,  $E_T(A-B)$  given by Eq. (15.83) is set equal to zero. Substitution of Eq. (15.81) into Eq. (15.83) gives

$$0 = \left[ \left( \frac{-e^2}{8\pi\epsilon_0 \sqrt{\frac{aa_0}{2C_1 C_2}}} \left[ c_1 c_2' \left( 2c_{BO} - c'_{BO} \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2C_1 C_2}}}{a - \sqrt{\frac{aa_0}{2C_1 C_2}}} - 1 \right] + E_T(\text{atom} - \text{atom}, msp^3, AO) \right) \right] \quad (15.84)$$

$$\left[ 1 + \sqrt{\frac{2\hbar \sqrt{\frac{c_{BO} C_{10} C_{20} e^2}{4\pi\epsilon_0 a^3}}}{m_e c^2}} + \frac{1}{2} \sqrt{\frac{c_{BO} \frac{c_1 c_2' e^2}{8\pi\epsilon_0 a^3} - \frac{c_{BO} e^2}{8\pi\epsilon_0 \left( a + \sqrt{\frac{aa_0}{2C_1 C_2}} \right)^3}}{\mu}} \right]$$

The vibrational energy-term of Eq. (15.84) is determined by the forces between the central field and the electrons and those between the nuclei (Eqs. (11.141-11.145)). The electron-central-field force and its derivative are given by

$$f(a) = -c_{BO} \frac{c_1 c_2' e^2}{4\pi\epsilon_0 a^3} \quad (15.85)$$

and

$$f'(a) = 2c_{BO} \frac{c_1 c_2' e^2}{4\pi\epsilon_0 a^3} \quad (15.86)$$

The nuclear repulsion force and its derivative are given by

$$f(a+c') = \frac{e^2}{8\pi\epsilon_0 (a+c')^2} \quad (15.87)$$

and

$$f'(a+c') = -\frac{e^2}{4\pi\epsilon_0 (a+c')^3} \quad (15.88)$$

such that the angular frequency of the oscillation is given by

$$\omega = \sqrt{\frac{\left[ \frac{-3}{a} f(a) - f'(a) \right]}{\mu}} = \sqrt{\frac{k}{m_e}} = \sqrt{\frac{c_{BO} \frac{c_1 c_2' e^2}{4\pi\epsilon_0 a^3} - \frac{e^2}{8\pi\epsilon_0 (a+c')^2}}{\mu}} \quad (15.89)$$

Since both terms of  $\bar{E}_{osc} = \bar{E}_D + \bar{E}_{Kvib}$  are small due to the large values of  $a$  and  $c'$ , to very good approximation, a convenient form of Eq. (15.84) which is evaluated to determine the bond angles of functional groups is given by

$$0 = \left[ \left( \frac{-e^2}{8\pi\epsilon_0 \sqrt{\frac{aa_0}{2C_1 C_2}}} \left[ c_1 c_2' \left( 2 - \frac{a_0}{a} \right) \ln \frac{a + \sqrt{\frac{aa_0}{2C_1 C_2}} - 1}{a - \sqrt{\frac{aa_0}{2C_1 C_2}}} + E_r(\text{atom} - \text{atom}, msp^3, AO) \right] \right) \right. \\ \left. \left[ 1 + \sqrt{\frac{2\hbar \sqrt{\frac{c_1 e^2}{4\pi\epsilon_0 a^3}}}{m_e c^2}} + \frac{1}{2} \hbar \sqrt{\frac{\frac{c_1 e^2}{8\pi\epsilon_0 a^3} - \frac{e^2}{8\pi\epsilon_0 \left( a + \sqrt{\frac{aa_0}{2C_1 C_2}} \right)^3}}{\mu}} \right] \right] \quad (15.90)$$

From the energy relationship given by Eq. (15.90) and the relationship between the axes given by Eqs. (15.2-15.5), the dimensions of the  $A-B$  MO can be solved. The most convenient way to solve Eq. (15.90) is by the reiterative technique using a computer.

A factor  $c_2$  of a given atom in the determination of  $c_2'$  for calculating the zero of the total  $A-B$  bond energy is typically given by Eqs. (15.62-15.65). In the case of a  $H-H$  terminal bond of an alkyl or alkenyl group,  $c_2'$  is typically the ratio of  $c_2$  of Eq. (15.62) for the  $H-H$  bond which is one and  $c_2$  of the carbon of the corresponding  $C-H$  bond:

$$c'_2 = \frac{1}{c_2(C2sp^3)} = \frac{13.605804 \text{ eV}}{E_{Coulomb}(C-H \text{ } C2sp^3)} \quad (15.91)$$

In the case of the determination of the bond angle of the  $ACH$  MO comprising a linear combination of  $C-A$ -bond and  $C-H$ -bond MOs where  $A$  and  $C$  are general,  $C$  is the central atom, and  $c_2$  for an atom is given by Eqs. (15.62-15.70),  $c'_2$  of the  $A-H$  terminal bond is typically the ratio of  $c_2$  of the  $A$  atom for the  $A-H$  terminal bond and  $c_2$  of the  $C$  atom of the corresponding  $C-H$  bond:

$$c'_2 = \frac{c_2(A(A-H)msp^3)}{c_2(C(C-H)(msp^3))} \quad (15.92)$$

In the case of the determination of the bond angle of the  $COH$  MO of an alcohol comprising a linear combination of  $C-O$ -bond and  $O-H$ -bond MOs where  $C$ ,  $O$ , and  $H$  are carbon, oxygen, and hydrogen, respectively,  $c'_2$  of the  $C-H$  terminal bond is typically 0.91771 since the oxygen and hydrogen atoms are at the Coulomb potential of a proton and an electron (Eqs. (1.236) and (10.162), respectively) that is energy matched to the  $C2sp^3$  HO.

In the determination of the hybridization factor  $c'_2$  of Eq. (15.90) from Eqs. (15.62-15.70), the Coulombic energy,  $E_{Coulomb}(MO.atom,msp^3)$ , or the energy,  $E(MO.atom,msp^3)$ , the radius  $r_{A-B \text{ } AorBsp^3}$  of the  $A$  or  $B$  AO or HO of the heteroatom of the  $A-B$  terminal bond MO such as the  $C2sp^3$  HO of a terminal  $C-C$  bond is calculated using Eq. (15.32) by considering  $\sum E_{T_{mol}}(MO,2sp^3)$ , the total energy donation to each bond with which it participates in bonding as it forms the terminal bond. The Coulombic energy  $E_{Coulomb}(MO.atom,msp^3)$  of the outer electron of the  $atom \text{ } msp^3$  shell is given by Eq. (15.19).

In the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy  $E(magnetic)$  (Eq. (15.15)) at the initial radius  $r$  of the AO electron. Then, the energy  $E(MO.atom,msp^3)$  of the outer electron of the  $atom \text{ } msp^3$  shell is given by the sum of  $E_{Coulomb}(MO.atom,msp^3)$  and  $E(magnetic)$  (Eq. (15.20)).

In the specific case of the terminal bonding of two carbon atoms, the  $c_2$  factor of each carbon given by Eq. (15.62) is determined using the Coulombic energy  $E_{Coulomb}(C-C \text{ } C2sp^3)$  of the outer electron of the  $C2sp^3$  shell given by Eq. (15.19) with the

radius  $r_{C-C\ C2sp^3}$  of each  $C2sp^3$  HO of the terminal  $C-C$  bond calculated using Eq. (15.32)

by considering  $\sum E_{T_{mol}}(MO, 2sp^3)$ , the total energy donation to each bond with which it participates in bonding as it forms the terminal bond including the contribution of the methylene energy,  $0.92918\ eV$  (Eq. (14.513)), corresponding to the terminal  $C-C$  bond.

5 The corresponding  $E_T(atom - atom, msp^3.AO)$  in Eq. (15.90) is  $E_T(C - C\ C2sp^3) = -1.85836\ eV$ .

In the case that the terminal atoms are carbon or other heteroatoms, the terminal bond comprises a linear combination of the HOs or AOs; thus,  $c'_2$  is the average of the hybridization factors of the participating atoms corresponding to the normalized linear sum:

$$10 \quad c'_2 = \frac{1}{2} (c'_2(atom\ 1) + c'_2(atom\ 2)) \quad (15.93)$$

In the exemplary cases of  $C-C$ ,  $O-O$ , and  $N-N$  where  $C$  is carbon:

$$\begin{aligned} c'_2 &= \frac{1}{2} \left( \frac{\frac{e^2}{8\pi\epsilon_0 a_0}}{\frac{e^2}{8\pi\epsilon_0 r_{A-A\ A_1 AO/HO}}} + \frac{\frac{e^2}{8\pi\epsilon_0 a_0}}{\frac{e^2}{8\pi\epsilon_0 r_{A-A\ A_2 AO/HO}}} \right) \\ &= \frac{1}{2} \left( \frac{13.605804\ eV}{E_{Coulomb}(A - A.A_1 AO / HO)} + \frac{13.605804\ eV}{E_{Coulomb}(A - A.A_2 AO / HO)} \right) \end{aligned} \quad (15.94)$$

In the exemplary cases of  $C-N$ ,  $C-O$ , and  $C-S$ ,

$$c'_2 = \frac{1}{2} \left( \frac{13.605804\ eV}{E_{Coulomb}(C - B\ C2sp^3)} + c_2(C\ to\ B) \right) \quad (15.95)$$

15 where  $C$  is carbon and  $c_2(C\ to\ B)$  is the hybridization factor of Eqs. (15.52) and (15.84) that matches the energy of the atom  $B$  to that of the atom  $C$  in the group. For these cases, the corresponding  $E_T(atom - atom, msp^3.AO)$  term in Eq. (15.90) depends on the hybridization and bond order of the terminal atoms in the molecule, but typical values matching those used in the determination of the bond energies (Eq. (15.56)) are

$$\begin{aligned} 20 \quad E_T(C - O\ C2sp^3.O2p) &= -1.44915\ eV; & E_T(C - O\ C2sp^3.O2p) &= -1.65376\ eV; \\ E_T(C - N\ C2sp^3.N2p) &= -1.44915\ eV; & E_T(C - S\ C2sp^3.S2p) &= -0.72457\ eV; \\ E_T(O - O\ O2p.O2p) &= -1.44915\ eV; & E_T(O - O\ O2p.O2p) &= -1.65376\ eV; \end{aligned}$$



481

$$\begin{aligned}
E_T(N-N\ N2p.N2p) &= -1.44915\ eV; & E_T(N-O\ N2p.O2p) &= -1.44915\ eV; \\
E_T(F-F\ F2p.F2p) &= -1.44915\ eV; & E_T(Cl-Cl\ Cl3p.Cl3p) &= -0.92918\ eV; \\
E_T(Br-Br\ Br4p.Br4p) &= -0.92918\ eV; & E_T(I-I\ I5p.I5p) &= -0.36229\ eV; \\
E_T(C-F\ C2sp^3.F2p) &= -1.85836\ eV; & E_T(C-Cl\ C2sp^3.Cl3p) &= -0.92918\ eV; \\
5\ E_T(C-Br\ C2sp^3.Br4p) &= -0.72457\ eV; & E_T(C-I\ C2sp^3.I5p) &= -0.36228\ eV, \text{ and} \\
E_T(O-Cl\ O2p.Cl3p) &= -0.92918\ eV.
\end{aligned}$$

In the case that the terminal bond is  $X-X$  where  $X$  is a halogen atom,  $c_1$  is one, and  $c'_2$  is the average (Eq. (15.93)) of the hybridization factors of the participating halogen atoms given by Eqs. (15.62-15.63) where  $E_{Coulomb}(MO.atom,msp^3)$  is determined using Eq. (15.32) and  $E_{Coulomb}(MO.atom,msp^3) = 13.605804\ eV$  for  $X = I$ . The factor  $C_1$  of Eq. (15.90) is one for all halogen atoms. The factor  $C_2$  of fluorine is one since it is the only halogen wherein the ionization energy is greater than that  $13.605804\ eV$ , the magnitude of the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). For each of the other halogens,  $Cl$ ,  $Br$ , and  $I$ ,  $C_2$  is the hybridization factor of Eq. (15.52) given by Eq. (15.70) with  $c_2(1)$  being that of the halogen given by Eq. (15.68) that matches the valence energy of  $X$  ( $E_1(valence)$ ) to that of the  $C2sp^3$  HO ( $E_2(valence) = -14.63489\ eV$ , Eq. (15.25)) and to the hybridization of  $C2sp^3$  HO ( $c_2(2) = 0.91771$ , Eq. (13.430)).  $E_T(atom-atom,msp^3.AO)$  of Eq. (15.90) is the maximum for the participating atoms which is  $-1.44915\ eV$ ,  $-0.92918\ eV$ ,  $-0.92918\ eV$ , and  $-0.33582\ eV$  for  $F$ ,  $Cl$ ,  $Br$ , and  $I$ , respectively.

Consider the case that the terminal bond is  $C-X$  where  $C$  is a carbon atom and  $X$  is a halogen atom. The factors  $c_1$  and  $C_1$  of Eq. (15.90) are one for all halogen atoms. For  $X = F$ ,  $c'_2$  is the average (Eq. (15.95)) of the hybridization factors of the participating carbon and  $F$  atoms where  $c_2$  for carbon is given by Eq. (15.62) and  $c_2$  for fluorine matched to carbon is given by Eq. (15.70) with  $c_2(1)$  for the fluorine atom given by Eq. (15.68) that matches the valence energy of  $F$  ( $E_1(valence) = -17.42282\ eV$ ) to that of the  $C2sp^3$  HO

( $E_2(\text{valence}) = -14.63489 \text{ eV}$ , Eq. (15.25)) and to the hybridization of  $C2sp^3$  HO ( $c_2(2) = 0.91771$ , Eq. (13.430)). The factor  $C_2$  of fluorine is one since it is the only halogen wherein the ionization energy is greater than that  $13.605804 \text{ eV}$ , the magnitude of the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). For each of the other halogens,  $Cl$ ,  $Br$ , and  $I$ ,  $c'_2$  is the hybridization factor of the participating carbon atom since the halogen atom is energy matched to the carbon atom.  $C_2$  of the terminal-atom bond matches that used to determine the energies of the corresponding  $C-X$ -bond MO. Then,  $C_2$  is the hybridization factor of Eq. (15.52) given by Eq. (15.70) with  $c_2(1)$  for the halogen atom given by Eq. (15.68) that matches the valence energy of  $X$  ( $E_1(\text{valence})$ ) to that of the  $C2sp^3$  HO ( $E_2(\text{valence}) = -14.63489 \text{ eV}$ , Eq. (15.25)) and to the hybridization of  $C2sp^3$  HO ( $c_2(2) = 0.91771$ , Eq. (13.430)).  $E_T(\text{atom} - \text{atom}, msp^3.AO)$  of Eq. (15.90) is the maximum for the participating atoms which is  $-1.85836 \text{ eV}$ ,  $-0.92918 \text{ eV}$ ,  $-0.72457 \text{ eV}$ , and  $-0.33582 \text{ eV}$  for  $F$ ,  $Cl$ ,  $Br$ , and  $I$ , respectively.

Consider the case that the terminal bond is  $H-X$  corresponding to the angle of the atoms  $HCX$  where  $C$  is a carbon atom and  $X$  is a halogen atom. The factors  $c_1$  and  $C_1$  of Eq. (15.90) are 0.75 for all halogen atoms. For  $X = F$ ,  $c'_2$  is given by Eq. (15.69) with  $c_2$  of the participating carbon and  $F$  atoms given by Eq. (15.62) and Eq. (15.65), respectively. The factor  $C_2$  of fluorine is one since it is the only halogen wherein the ionization energy is greater than that  $13.605804 \text{ eV}$ , the magnitude of the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). For each of the other halogens,  $Cl$ ,  $Br$ , and  $I$ ,  $c'_2$  is also given by Eq. (15.69) with  $c_2$  of the participating carbon given by Eq. (15.62) and  $c_2$  of the participating  $X$  atom given by  $c_2 = 0.91771$  (Eq. (13.430)) since the  $X$  atom is energy matched to the  $C2sp^3$  HO. In these cases,  $C_2$  is given by Eq. (15.65) for the corresponding atom  $X$  where  $C_2$  matches the energy of the atom  $X$  to that of  $H$ .

Using the distance between the two atoms  $A$  and  $B$  of the general molecular group  $ACB$  when the total energy of the corresponding  $A-B$  MO is zero, the corresponding bond angle can be determined from the law of cosines:

$$s_1^2 + s_2^2 - 2s_1s_2\cos\theta = s_3^2 \quad (15.96)$$

With  $s_1 = 2c'_{C-A}$ , the internuclear distance of the  $C-A$  bond,  $s_2 = 2c'_{C-B}$ , the internuclear distance of each  $C-B$  bond, and  $s_3 = 2c'_{A-B}$ , the internuclear distance of the two terminal atoms, the bond angle  $\theta_{ACB}$  between the  $C-A$  and  $C-B$  bonds is given by

$$(2c'_{C-A})^2 + (2c'_{C-B})^2 - 2(2c'_{C-A})(2c'_{C-B})\cos\theta = (2c'_{A-B})^2 \quad (15.97)$$

$$5 \quad \theta_{ACB} = \cos^{-1} \left( \frac{(2c'_{C-A})^2 + (2c'_{C-B})^2 - (2c'_{A-B})^2}{2(2c'_{C-A})(2c'_{C-B})} \right) \quad (15.98)$$

Consider the exemplary structure  $C_b C_a (O_a) O_b$  wherein  $C_a$  is bound to  $C_b$ ,  $O_a$ , and  $O_b$ . In the general case that the three bonds are coplanar and two of the angles are known, say  $\theta_1$  and  $\theta_2$ , then the third  $\theta_3$  can be determined geometrically:

$$\theta_3 = 360 - \theta_1 - \theta_2 \quad (15.99)$$

10 In the general case that two of the three coplanar bonds are equivalent and one of the angles is known, say  $\theta_1$ , then the second and third can be determined geometrically:

$$\theta_2 = \theta_3 = \frac{(360 - \theta_1)}{2} \quad (15.100)$$

## ANGLES AND DISTANCES FOR AN MO THAT FORMS AN ISOSCELES

### 15 TRIANGLE

In the general case where the group comprises three  $A-B$  bonds having  $B$  as the central atom at the apex of a pyramidal structure formed by the three bonds with the  $A$  atoms at the base in the xy-plane. The  $C_{3v}$  axis centered on  $B$  is defined as the vertical or z-axis, and any two  $A-B$  bonds form an isosceles triangle. Then, the angle of the bonds and the distances  
20 from and along the z-axis are determined from the geometrical relationships given by Eqs. (13.412-13.416):

the distance  $d_{origin-B}$  from the origin to the nucleus of a terminal  $B$  atom is given by

$$d_{origin-B} = \frac{2c'_{B-B}}{2\sin 60^\circ} \quad (15.101)$$

the height along the z-axis from the origin to the  $A$  nucleus  $d_{height}$  is given by

$$25 \quad d_{height} = \sqrt{(2c'_{A-B})^2 - (d_{origin-B})^2}, \text{ and} \quad (15.102)$$

the angle  $\theta_v$  of each  $A-B$  bond from the z-axis is given by

$$\theta_v = \tan^{-1} \left( \frac{d_{\text{origin}-B}}{d_{\text{height}}} \right) \quad (15.103)$$

Consider the case where the central atom  $B$  is further bound to a fourth atom  $C$  and the  $B-C$  bond is along the z-axis. Then, the bond  $\theta_{\angle ABC}$  given by Eq. (14.206) is

$$\theta_{\angle ABC} = 180 - \theta_v \quad (15.104)$$

## DIHEDRAL ANGLE

Consider the plane defined by a general  $ACA$  MO comprising a linear combination of two  $C-A$ -bond MOs where  $C$  is the central atom. The dihedral angle  $\theta_{\angle BCI/ACA}$  between the  $ACA$ -plane and a line defined by a third bond with  $C$ , specifically that corresponding to a  $C-B$ -bond MO, is calculated from the bond angle  $\theta_{\angle ACA}$  and the distances between the  $A$ ,  $B$ , and  $C$  atoms. The distance  $d_1$  along the bisector of  $\theta_{\angle ACA}$  from  $C$  to the internuclear-distance line between  $A$  and  $A$ ,  $2c'_{A-A}$ , is given by

$$d_1 = 2c'_{C-A} \cos \frac{\theta_{\angle ACA}}{2} \quad (15.105)$$

where  $2c'_{C-A}$  is the internuclear distance between  $A$  and  $C$ . The atoms  $A$ ,  $A$ , and  $B$  define the base of a pyramid. Then, the pyramidal angle  $\theta_{\angle ABA}$  can be solved from the internuclear distances between  $A$  and  $A$ ,  $2c'_{A-A}$ , and between  $A$  and  $B$ ,  $2c'_{A-B}$ , using the law of cosines (Eq. (15.98)):

$$\theta_{\angle ABA} = \cos^{-1} \left( \frac{(2c'_{A-B})^2 + (2c'_{A-B})^2 - (2c'_{A-A})^2}{2(2c'_{A-B})(2c'_{A-B})} \right) \quad (15.106)$$

Then, the distance  $d_2$  along the bisector of  $\theta_{\angle ABA}$  from  $B$  to the internuclear-distance line  $2c'_{A-A}$ , is given by

$$d_2 = 2c'_{A-B} \cos \frac{\theta_{\angle ABA}}{2} \quad (15.107)$$

The lengths  $d_1$ ,  $d_2$ , and  $2c'_{C-B}$  define a triangle wherein the angle between  $d_1$  and the internuclear distance between  $B$  and  $C$ ,  $2c'_{C-B}$ , is the dihedral angle  $\theta_{\angle BCI/ACA}$  that can be solved using the law of cosines (Eq. (15.98)):

$$\theta_{\angle BC/ACA} = \cos^{-1} \left( \frac{d_1^2 + (2c'_{C-B})^2 - d_2^2}{2d_1(2c'_{B-C})} \right) \quad (15.108)$$

## SOLUTION OF GEOMETRICAL AND ENERGY PARAMETERS OF MAJOR FUNCTIONAL GROUPS AND CORRESPONDING ORGANIC MOLECULES

The exemplary molecules given in the following sections were solved using the solutions of organic chemical functional groups as basis elements wherein the structures and energies were linearly added to achieve the molecular solutions. Each functional group can be treated as a building block to form any desired molecular solution from the corresponding linear combination. Each functional group element was solved using the atomic orbital and hybrid orbital spherical orbitals solutions bridged by molecular orbitals comprised of the  $H_2$ -type prolate spheroidal solution given in the Nature of the Chemical Bond of Hydrogen-Type Molecules section. The energy of each MO was matched at the HO or AO by matching the hybridization and total energy of the MO to the AOs and HOs. The energy  $E_{mag}$  (e.g. given by Eq. (15.58)) for a  $C2sp^3$  HO and Eq.(15.59) for an  $O2p$  AO) was subtracted for each set of unpaired electrons created by bond breakage.

The bond energy is not equal to the component energy of each bond as it exists in the molecule; although, they are close. The total energy of each group is its contribution to the total energy of the molecule as a whole. The determination of the bond energies for the creation of the separate parts must take into account the energy of the formation of any radicals and any redistribution of charge density within the pieces and the corresponding energy change with bond cleavage. Also, the vibrational energy in the transition state is dependent on the other groups that are bound to a given functional group. This will effect the functional-group energy. But, because the variations in the energy based on the balance of the molecular composition are typically of the order of a few hundreds of electron volts at most, they were neglected.

The energy of each functional-group MO bonding to a given carbon HO is independently matched to the HO by subtracting the contribution to the change in the energy of the HO from the total MO energy given by the sum of the MO contributions and  $E(C,2sp^3) = -14.63489 \text{ eV}$  (Eq. (13.428)). The intercept angles are determined from Eqs.

(15.71-15.78) using the final radius of the HO of each atom. The final carbon-atom radius is determined using Eqs. (15.32) wherein the sum of the energy contributions of each atom to all the MOs in which it participates in bonding is determined. This final radius is used in Eqs. (15.19) and (15.20) to calculate the final valence energy of the HO of each atom at the  
5 corresponding final radius. The radius of any bonding heteroatom that contributes to a MO is calculated in the same manner, and the energy of its outermost shell is matched to that of the MO by the hybridization factor between the carbon-HO energy and the energy of the heteroatomic shell. The donation of electron density to the AOs and HOs reduces the energy. The donation of the electron density to the MO's at each AO or HO is that which causes the  
10 resulting energy to be divided equally between the participating AOs or HOs to achieve energy matching.

The molecular solutions can be used to design synthetic pathways and predict product yields based on equilibrium constants calculated from the heats of formation. New stable compositions of matter can be predicted as well as the structures of combinatorial chemistry  
15 reactions. Further important pharmaceutical applications include the ability to graphically or computationally render the structures of drugs that permit the identification of the biologically active parts of the molecules to be identified from the common spatial charge-density functions of a series of active molecules. Drugs can be designed according to geometrical parameters and bonding interactions with the data of the structure of the active site of the  
20 drug.

To calculate conformations, folding, and physical properties, the exact solutions of the charge distributions in any given molecule are used to calculate the fields, and from the fields, the interactions between groups of the same molecule or between groups on different molecules are calculated wherein the interactions are distance and relative orientation  
25 dependent. The fields and interactions can be determined using a finite-element-analysis approach of Maxwell's equations.

## AROMATIC AND HETEROCYCLIC COMPOUNDS

Aromatic and heterocyclic molecules comprise at least one of an aromatic or a cyclic conjugated alkene functional group. The latter was described in the Cyclic and Conjugated Alkenes section. The aromatic bond is uniquely stable and requires the sharing of the electrons of multiple  $H_2$ -type MOs. The results of the derivation of the parameters of the benzene molecule given in the Benzene Molecule ( $C_6H_6$ ) section can be generalized to any aromatic function group(s) of aromatic and heterocyclic compounds.

$C_6H_6$  can be considered a linear combination of three ethylene molecules wherein a  $C-H$  bond of each  $CH_2$  group of  $H_2C=CH_2$  is replaced by a  $C=C$  bond to form a six-member ring of carbon atoms. The solution of the ethylene molecule is given in the Ethylene Molecule ( $CH_2CH_2$ ) section. The radius  $r_{ethylene 2sp^3}$  ( $0.85252a_0$ ) of the  $C2sp^3$  shell of ethylene calculated from the Coulombic energy is given by Eq. (14.244). The Coulombic energy  $E_{Coulomb}(C_{ethylene}, 2sp^3)$  ( $-15.95955 eV$ ) of the outer electron of the  $C2sp^3$  shell is given by Eq. (14.245). The energy  $E(C_{ethylene}, 2sp^3)$  ( $-15.76868 eV$ ) of the outer electron of the  $C2sp^3$  shell is given by Eq. (14.246).  $E_T(C=C, 2sp^3)$  ( $-1.13380 eV$ ) (Eq. (14.247), the energy change of each  $C2sp^3$  shell with the formation of the  $C=C$ -bond MO is given by the difference between  $E(C_{ethylene}, 2sp^3)$  and  $E(C, 2sp^3)$ .  $C_6H_6$  can be solved using the same principles as those used to solve ethylene wherein the  $2s$  and  $2p$  shells of each  $C$  hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Each  $2sp^3$  HO of each carbon atom initially has four unpaired electrons. Thus, the 6  $H$  atomic orbitals (AOs) of benzene contribute six electrons and the six  $sp^3$ -hybridized carbon atoms contribute twenty-four electrons to form six  $C-H$  bonds and six  $C=C$  bonds. Each  $C-H$  bond has two paired electrons with one donated from the  $H$  AO and the other from the  $C2sp^3$  HO. Each  $C=C$  bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from two sets of two  $C2sp^3$  HOs of the participating carbon atoms. Each  $C-H$  and each  $C=C$  bond comprises a linear combination of one and two diatomic  $H_2$ -type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section, respectively.

Consider the case where three sets of  $C=C$ -bond MOs form bonds between the two carbon atoms of each molecule to form a six-member ring such that the six resulting bonds comprise eighteen paired electrons. Each bond comprises a linear combination of two MOs wherein each comprises two  $C2sp^3$  HOs and 75% of a  $H_2$ -type ellipsoidal MO divided between the  $C2sp^3$  HOs:

$$\left( \begin{array}{l} 3(2 C2sp^3 + 0.75 H_2 MO) \rightarrow 3 \overset{4e}{(C=C)} - \text{ethylene-type-bond MO} \\ \rightarrow 6 \overset{3e}{(C=C)} - \text{bond MO of benzene} \end{array} \right) \quad (15.142)$$

The linear combination of each  $H_2$ -type ellipsoidal MO with each  $C2sp^3$  HO further comprises an excess 25% charge-density contribution per bond from each  $C2sp^3$  HO to the  $C=C$ -bond MO to achieve an energy minimum. Thus, the dimensional parameters of each bond  $C=C$ -bond are determined using Eqs. (15.42) and (15.1-15.5) in a form that are the same equations as those used to determine the same parameters of the  $C=C$ -bond MO of ethylene (Eqs. (14.242-14.268)) while matching the boundary conditions of the structure of benzene.

Hybridization with 25% electron donation to each  $C=C$ -bond gives rise to the  $C_{benzene}2sp^3$  HO-shell Coulombic energy  $E_{Coulomb}(C_{benzene}, 2sp^3)$  given by Eq. (14.245). To meet the equipotential condition of the union of the six  $C2sp^3$  HOs,  $c_2$  and  $C_2$  of Eq. (15.42) for the aromatic  $C=C$ -bond MO is given by Eq. (15.62) as the ratio of 15.95955 eV, the magnitude of  $E_{Coulomb}(C_{benzene}, 2sp^3)$  (Eq. (14.245)), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of  $H$  (Eq. (1.243)):

$$C_2(benzeneC2sp^3HO) = c_2(benzeneC2sp^3HO) = \frac{13.605804 \text{ eV}}{15.95955 \text{ eV}} = 0.85252 \quad (15.143)$$

The energies of each  $C=C$  bond of benzene are also determined using the same equations as those of ethylene (Eqs. (14.251-14.253) and (14.319-14.333) with the parameters of

benzene. Ethylene serves as a basis element for the  $C=C$  bonding of benzene wherein each of the six  $C=C$  bonds of benzene comprises  $(0.75)(4) = 3$  electrons according to Eq. (15.142).

The total energy of the bonds of the eighteen electrons of the  $C=C$  bonds of benzene,  $E_T(C_6H_6, C=C)$ , is given by  $(6)(0.75)$  times  $E_{T+osc}(C=C)$  (Eq. (14.492)), the total energy of

the  $C=C$ -bond MO of benzene including the Doppler term, minus eighteen times  $E(C, 2sp^3)$  (Eq. (14.146)), the initial energy of each  $C2sp^3$  HO of each  $C$  that forms the  $C=C$  bonds of bond order two. Thus, the total energy of the six  $C=C$  bonds of benzene with three electron per aromatic bond given by Eq. (14.493) is

$$\begin{aligned} E_T\left(C_6H_6, C=C\right) &= (6)(0.75)E_{T+osc}(C=C) - (6)(3)E(C, 2sp^3) \\ &= (6)(0.75)(-66.05796 \text{ eV}) - 18(-14.63489 \text{ eV}) \\ &= -297.26081 \text{ eV} - (-263.42798 \text{ eV}) \\ &= -33.83284 \text{ eV} \end{aligned} \quad (15.144)$$

The results of benzene can be generalized to the class of aromatic and heterocyclic compounds.  $E_{hv}$  of an aromatic bond is given by  $E_T(H_2)$  (Eqs. (11.212) and (14.486)), the maximum total energy of each  $H_2$ -type MO such that

$$\bar{E}_{osc} = n_1(\bar{E}_D + \bar{E}_{Kvib}) = n_1\left[-31.63536831 \text{ eV} \sqrt{\frac{2\bar{E}_K}{Mc^2}} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}\right] \quad (15.145)$$

The factor of 0.75 corresponding to the three electrons per aromatic bond of bond order two given in the Benzene Molecule ( $C_6H_6$ ) section modifies Eqs. (15.52-15.56). Multiplication of



the total energy given by Eq. (15.55) by  $f_1 = 0.75$  with the substitution of Eq. (15.145) gives the total energy of the aromatic bond:

$$E_T(\text{Group}) = f_1 \left[ \begin{array}{l} E(\text{basis energies}) + E_T(\text{atom} - \text{atom}, msp^3.AO) \\ -31.63536831 \text{ eV} \sqrt{\frac{2\hbar \sqrt{\frac{C_{10} C_{20} e^2}{4\pi\epsilon_0 R^3}}}{m_e}} + n_1 \bar{E}_{Kvib} + c_3 \frac{8\pi\mu_o \mu_B^2}{r^3} \end{array} \right] \quad (15.146)$$

- 5 The total bond energy of the aromatic group  $E_D(\text{Group})$  is the negative difference of the total energy of the group (Eq. (15.146)) and the total energy of the starting species given by the sum of  $c_4 E_{\text{initial}}(c_4 \text{ AO} / \text{HO})$  and  $c_5 E_{\text{initial}}(c_5 \text{ AO} / \text{HO})$ :

$$E_D(\text{Group}) = - \left[ \begin{array}{l} f_1 \left[ \begin{array}{l} E(\text{basis energies}) + E_T(\text{atom} - \text{atom}, msp^3.AO) \\ -31.63536831 \text{ eV} \sqrt{\frac{2\hbar \sqrt{\frac{C_{10} C_{20} e^2}{4\pi\epsilon_0 R^3}}}{m_e}} + n_1 \bar{E}_{Kvib} + c_3 \frac{8\pi\mu_o \mu_B^2}{r^3} \end{array} \right] \\ - (c_4 E_{\text{initial}}(\text{AO} / \text{HO}) + c_5 E_{\text{initial}}(c_5 \text{ AO} / \text{HO})) \end{array} \right] \quad (15.147)$$

Since there are three electrons per aromatic bond,  $c_4$  is three times the number of aromatic  
10 bonds.

Benzene can also be considered as comprising chemical bonds between six  $CH$  radicals wherein each radical comprises a chemical bond between carbon and hydrogen atoms. The solution of the parameters of  $CH$  is given in the Hydrogen Carbide ( $CH$ ) section. Those of the benzene are given in the Benzene Molecule ( $C_6H_6$ ) section. The energy components of  $V_e$ ,  $V_p$ ,

- 15  $T$ ,  $V_m$ , and  $E_T$  are the same as those of the hydrogen carbide radical, except that  $E_T(C = C, 2sp^3) = -1.13379 \text{ eV}$  (Eq. (14.247)) is subtracted from  $E_T(CH)$  of Eq. (13.495) to match the energy of each  $C-H$ -bond MO to the decrease in the energy of the corresponding  $C2sp^3$  HO. In the corresponding generalization of the aromatic  $CH$  group, the geometrical parameters are determined using Eq. (15.42) and Eqs. (15.1-15.5) with  
20  $E_T(\text{atom} - \text{atom}, msp^3.AO) = -1.13379 \text{ eV}$ .

The total energy of the benzene  $C-H$ -bond MO,  $E_{T_{\text{benzene}}}(C-H)$ , given by Eq. (14.467) is the sum of  $0.5E_T(C = C, 2sp^3)$ , the energy change of each  $C2sp^3$  shell per single bond due to

the decrease in radius with the formation of the corresponding  $C=C$ -bond MO (Eq. (14.247)), and  $E_{T_{\text{benzene}}}(CH)$ , the  $\sigma$  MO contribution given by Eq. (14.441). In the corresponding

- 25 generalization of the aromatic  $CH$  group, the energy parameters are determined using Eqs.

(15.146-15.147) with  $f_1 = 1$  and  $E_T(\text{atom} - \text{atom}, msp^3.AO) = \frac{-1.13379 \text{ eV}}{2}$ . Thus, the energy

contribution to the single aromatic  $CH$  bond is one half that of the  $C=C$  double bond contribution. This matches the energies of the  $CH$  and  $C=C$  aromatic groups, conserves the electron number with the equivalent charge density as that of  $s=1$  in Eqs. (15.18-15.21), and further gives a minimum energy for the molecule. Breakage of the aromatic  $C=C$  bonds to give  $CH$  groups creates unpaired electrons in these fragments that corresponds to  $c_3=1$  in Eq. (15.56) with  $E_{mag}$  given by Eq. (15.58).

Each of the  $C-H$  bonds of benzene comprises two electrons according to Eq. (14.439). From the energy of each  $C-H$  bond,  $-E_{D_{benzene}}(^{12}CH)$  (Eq. (14.477)), the total energy of the twelve electrons of the six  $C-H$  bonds of benzene,  $E_T(C_6H_6, C-H)$ , given by Eq. (14.494) is

$$E_T(C_6H_6, C-H) = (6)(-E_{D_{benzene}}(^{12}CH)) = 6(-3.90454 \text{ eV}) = -23.42724 \text{ eV} \quad (15.148)$$

The total bond dissociation energy of benzene,  $E_D(C_6H_6)$ , given by Eq. (14.495) is the negative sum of  $E_T(C_6H_6, C=C)$  (Eq. (14.493)) and  $E_T(C_6H_6, C-H)$  (Eq. (14.494)):

$$\begin{aligned} E_D(C_6H_6) &= -\left(E_T(C_6H_6, C=C) + E_T(C_6H_6, C-H)\right) \\ &= -((-33.83284 \text{ eV}) + (-23.42724 \text{ eV})) \\ &= 57.2601 \text{ eV} \end{aligned} \quad (15.149)$$

Using the parameters given in Tables 15.214 and 15.216 in the general equations (Eqs. (15.42), (15.1-15.5), and (15.146-15.147)) reproduces the results for benzene given in the Benzene Molecule ( $C_6H_6$ ) section as shown in Tables 15.214 and 15.216.

The symbols of the functional groups of aromatics and hertocyclics are given in Table 15.213. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aromatics and hertocyclics are given in Tables 15.214, 15.215, and 15.216, respectively. The total energy of benzene given in Table 15.217 was calculated as the sum over the integer multiple of each  $E_{D(Group)}$  of Table 15.216 corresponding to functional-group composition of the molecule. The bond angle parameters of benzene determined using Eqs. (15.79-15.108) are given in Table 15.218.

Table 15.213. The symbols of functional groups of aromatics and hertocyclics.

| Functional Group   | Group Symbol |
|--------------------|--------------|
| CC (aromatic bond) | $C=C$        |
| CH (aromatic)      | $CH$ (i)     |

Table 15.214. The geometrical bond parameters of aromatics and hertocyclics and experimental values [1].

| Parameter                         | $\overset{3e}{C=C}$<br>Group | $CH$<br>Group      |
|-----------------------------------|------------------------------|--------------------|
| $a \ (a_0)$                       | 1.47348                      | 1.60061            |
| $c' \ (a_0)$                      | 1.31468                      | 1.03299            |
| Bond Length $2c' \ (\square)$     | 1.39140                      | 1.09327            |
| Exp. Bond Length<br>( $\square$ ) | 1.399<br>(benzene)           | 1.101<br>(benzene) |
| $b, c \ (a_0)$                    | 0.66540                      | 1.22265            |
| $e$                               | 0.89223                      | 0.64537            |

5 Table 15.216. The energy parameters (eV) of functional groups of aromatics and heterocyclics.

| Parameters                          | $\overset{3e}{C=C}$<br>Group | $CH$<br>Group |
|-------------------------------------|------------------------------|---------------|
| $f_1$                               | 0.75                         | 1             |
| $n_1$                               | 2                            | 1             |
| $n_2$                               | 0                            | 0             |
| $n_3$                               | 0                            | 0             |
| $C_1$                               | 0.5                          | 0.75          |
| $C_2$                               | 0.85252                      | 1             |
| $c_1$                               | 1                            | 1             |
| $c_2$                               | 0.85252                      | 0.91771       |
| $c_3$                               | 0                            | 1             |
| $c_4$                               | 3                            | 1             |
| $c_5$                               | 0                            | 1             |
| $C_{1o}$                            | 0.5                          | 0.75          |
| $C_{2o}$                            | 0.85252                      | 1             |
| $V_e \ (eV)$                        | -101.12679                   | -37.10024     |
| $V_p \ (eV)$                        | 20.69825                     | 13.17125      |
| $T \ (eV)$                          | 34.31559                     | 11.58941      |
| $V_m \ (eV)$                        | -17.15779                    | -5.79470      |
| $E_{(AO/HO)} \ (eV)$                | 0                            | -14.63489     |
| $\Delta E_{H_2MO \ (AO/HO)} \ (eV)$ | 0                            | -1.13379      |

|                                    |                 |                         |
|------------------------------------|-----------------|-------------------------|
| $E_T (AO/HO) (eV)$                 | 0               | -13.50110               |
| $E_T (H_2MO) (eV)$                 | -63.27075       | -31.63539               |
| $E_T (atom - atom, msp^3 AO) (eV)$ | -2.26759        | -0.56690                |
| $E_T (MO) (eV)$                    | -65.53833       | -32.20226               |
| $\omega (10^{15} rad / s)$         | 49.7272         | 26.4826                 |
| $E_K (eV)$                         | 32.73133        | 17.43132                |
| $\bar{E}_D (eV)$                   | -0.35806        | -0.26130                |
| $\bar{E}_{Kvib} (eV)$              | 0.19649<br>[49] | 0.35532<br>Eq. (13.458) |
| $\bar{E}_{osc} (eV)$               | -0.25982        | -0.08364                |
| $E_{mag} (eV)$                     | 0.14803         | 0.14803                 |
| $E_T (Group) (eV)$                 | -49.54347       | -32.28590               |
| $E_{initial} (e_4 AO/HO) (eV)$     | -14.63489       | -14.63489               |
| $E_{initial} (e_5 AO/HO) (eV)$     | 0               | -13.59844               |
| $E_D (Group) (eV)$                 | 5.63881         | 3.90454                 |

Table 15.215. The MO to HO intercept geometrical bond parameters of benzene.  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{msp}^3 \text{AO})$ .

| Bond              | Atom  | $E_r$<br>(eV)<br>Bond 1 | $E_r$<br>(eV)<br>Bond 2 | $E_r$<br>(eV)<br>Bond 3 | $E_r$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>$C2sp^3$<br>(eV) | $r_{\text{initial}}$<br>( $a_0$ ) | $r_{\text{final}}$<br>( $a_0$ ) |
|-------------------|-------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------------------------|-----------------------------------|---------------------------------|
| $C-H$ (CH)        | C     | -0.85035                | -0.85035                | -0.56690                | 0                       | -153.88327                                | 0.91771                           | 0.79597                         |
| ${}^{3e}C=HC_a=C$ | $C_a$ | -0.85035                | -0.85035                | -0.56690                | 0                       | -153.88327                                | 0.91771                           | 0.79597                         |

| Bond              | $E_{\text{Conlamb}}$<br>( $C2sp^3$ )(eV)<br>Final | $E(C2sp^3)$<br>(eV)<br>Final | $\theta'$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | $d_1$<br>( $a_0$ ) | $d_2$<br>( $a_0$ ) |
|-------------------|---------------------------------------------------|------------------------------|---------------------------|----------------------------|----------------------------|--------------------|--------------------|
| $C-H$ (CH)        | -17.09334                                         | -16.90248                    | 74.42                     | 105.58                     | 38.84                      | 1.24678            | 0.21379            |
| ${}^{3e}C=HC_a=C$ | -17.09334                                         | -16.90248                    | 134.24                    | 45.76                      | 58.98                      | 0.75935            | 0.55533            |

Table 15.217. The total bond energies of benzene calculated using the functional group composition and the energies of Table 15.216 compared to the experimental values [2].

| Formula  | Name    | ${}^{3e}C=C$ | CH | Calculated<br>Total Bond Energy<br>(eV) | Experimental<br>Total Bond Energy (eV) | Relative Error |
|----------|---------|--------------|----|-----------------------------------------|----------------------------------------|----------------|
| $C_6H_6$ | Benzene | 6            | 6  | 57.26008                                | 57.26340                               | 0.00006        |

Table 15.218. The bond angle parameters of benzene and experimental values [1].  $E_r$  is  $E_r(atom - atom, msp^3 AO)$ .

| Atoms of Angle             | $2c'$<br>Bond 1<br>( $a_0$ ) | $2c'$<br>Bond 2<br>( $a_0$ ) | $2c'$<br>Terminal<br>Atoms<br>( $a_0$ ) | $E_{Coulombic}$<br>Atom 1 | Atom 1<br>Hybridization<br>Designation<br>(Table<br>15.3.A) | $E_{Coulombic}$<br>Atom 2 | Atom 2<br>Hybridization<br>Designation<br>(Table<br>15.3.A) | $c_2$<br>Atom 1 | $c_2$<br>Atom 2 | $C_1$ | $C_2$ |
|----------------------------|------------------------------|------------------------------|-----------------------------------------|---------------------------|-------------------------------------------------------------|---------------------------|-------------------------------------------------------------|-----------------|-----------------|-------|-------|
| $\angle CCC$<br>(aromatic) | 2.62936                      | 2.62936                      | 4.5585                                  | -17.17218                 | 34                                                          | -17.17218                 | 34                                                          | 0.79232         | 0.79232         | 1     | 1     |
| $\angle CCH$<br>(aromatic) |                              |                              |                                         |                           |                                                             |                           |                                                             |                 |                 |       |       |

| Atoms of Angle             | $c_1$ | $c'_2$  | $E_r$<br>(eV) | $\theta_v$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | Cal. $\theta$<br>( $^\circ$ ) | Exp. $\theta$<br>( $^\circ$ ) |
|----------------------------|-------|---------|---------------|----------------------------|----------------------------|----------------------------|-------------------------------|-------------------------------|
| $\angle CCC$<br>(aromatic) | 1     | 0.79232 | -1.85836      |                            |                            |                            | 120.19                        | 120 [50-52]<br>(benzene)      |
| $\angle CCH$<br>(aromatic) |       |         |               |                            | 120.19                     |                            | 119.91                        | 120 [50-52]<br>(benzene)      |

Table 1.1. The calculated and experimental total bond energies of n-alkanes using closed-form equations having integers and fundamental constants only.

| Formula                         | Name       | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|---------------------------------|------------|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>3</sub> H <sub>8</sub>   | Propane    | 41.46896                                | 41.434                                    | -0.00085       |
| C <sub>4</sub> H <sub>10</sub>  | Butane     | 53.62666                                | 53.61                                     | -0.00036       |
| C <sub>5</sub> H <sub>12</sub>  | Pentane    | 65.78436                                | 65.77                                     | -0.00017       |
| C <sub>6</sub> H <sub>14</sub>  | Hexane     | 77.94206                                | 77.93                                     | -0.00019       |
| C <sub>7</sub> H <sub>16</sub>  | Heptane    | 90.09976                                | 90.09                                     | -0.00013       |
| C <sub>8</sub> H <sub>18</sub>  | Octane     | 102.25746                               | 102.25                                    | -0.00006       |
| C <sub>9</sub> H <sub>20</sub>  | Nonane     | 114.41516                               | 114.40                                    | -0.00012       |
| C <sub>10</sub> H <sub>22</sub> | Decane     | 126.57286                               | 126.57                                    | -0.00003       |
| C <sub>11</sub> H <sub>24</sub> | Undecane   | 138.73056                               | 138.736                                   | 0.00004        |
| C <sub>12</sub> H <sub>26</sub> | Dodecane   | 150.88826                               | 150.88                                    | -0.00008       |
| C <sub>18</sub> H <sub>38</sub> | Octadecane | 223.83446                               | 223.85                                    | 0.00008        |

Table 1.2. The calculated and experimental total bond energies of branched alkanes using closed-form equations having integers and fundamental constants only.

| Formula                        | Name                       | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|--------------------------------|----------------------------|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>4</sub> H <sub>10</sub> | Isobutane                  | 53.69922                                | 53.695                                    | -0.00007       |
| C <sub>5</sub> H <sub>12</sub> | Isopentane                 | 65.85692                                | 65.843                                    | -0.00021       |
| C <sub>5</sub> H <sub>12</sub> | Neopentane                 | 65.86336                                | 65.992                                    | 0.00195        |
| C <sub>6</sub> H <sub>14</sub> | 2-Methylpentane            | 78.01462                                | 78.007                                    | -0.00010       |
| C <sub>6</sub> H <sub>14</sub> | 3-Methylpentane            | 78.01462                                | 77.979                                    | -0.00046       |
| C <sub>6</sub> H <sub>14</sub> | 2,2-Dimethylbutane         | 78.02106                                | 78.124                                    | 0.00132        |
| C <sub>6</sub> H <sub>14</sub> | 2,3-Dimethylbutane         | 77.99581                                | 78.043                                    | 0.00061        |
| C <sub>7</sub> H <sub>16</sub> | 2-Methylhexane             | 90.17232                                | 90.160                                    | -0.00014       |
| C <sub>7</sub> H <sub>16</sub> | 3-Methylhexane             | 90.17232                                | 90.127                                    | -0.00051       |
| C <sub>7</sub> H <sub>16</sub> | 3-Ethylpentane             | 90.17232                                | 90.108                                    | -0.00072       |
| C <sub>7</sub> H <sub>16</sub> | 2,2-Dimethylpentane        | 90.17876                                | 90.276                                    | 0.00107        |
| C <sub>7</sub> H <sub>16</sub> | 2,2,3-Trimethylbutane      | 90.22301                                | 90.262                                    | 0.00044        |
| C <sub>7</sub> H <sub>16</sub> | 2,4-Dimethylpentane        | 90.24488                                | 90.233                                    | -0.00013       |
| C <sub>7</sub> H <sub>16</sub> | 3,3-Dimethylpentane        | 90.17876                                | 90.227                                    | 0.00054        |
| C <sub>8</sub> H <sub>18</sub> | 2-Methylheptane            | 102.33002                               | 102.322                                   | -0.00008       |
| C <sub>8</sub> H <sub>18</sub> | 3-Methylheptane            | 102.33002                               | 102.293                                   | -0.00036       |
| C <sub>8</sub> H <sub>18</sub> | 4-Methylheptane            | 102.33002                               | 102.286                                   | -0.00043       |
| C <sub>8</sub> H <sub>18</sub> | 3-Ethylhexane              | 102.30169                               | 102.274                                   | -0.00027       |
| C <sub>8</sub> H <sub>18</sub> | 2,2-Dimethylhexane         | 102.33646                               | 102.417                                   | 0.00079        |
| C <sub>8</sub> H <sub>18</sub> | 2,3-Dimethylhexane         | 102.31121                               | 102.306                                   | -0.00005       |
| C <sub>8</sub> H <sub>18</sub> | 2,4-Dimethylhexane         | 102.40258                               | 102.362                                   | -0.00040       |
| C <sub>8</sub> H <sub>18</sub> | 2,5-Dimethylhexane         | 102.40258                               | 102.396                                   | -0.00006       |
| C <sub>8</sub> H <sub>18</sub> | 3,3-Dimethylhexane         | 102.33646                               | 102.369                                   | 0.00032        |
| C <sub>8</sub> H <sub>18</sub> | 3,4-Dimethylhexane         | 102.31121                               | 102.296                                   | -0.00015       |
| C <sub>8</sub> H <sub>18</sub> | 3-Ethyl-2-methylpentane    | 102.31121                               | 102.277                                   | -0.00033       |
| C <sub>8</sub> H <sub>18</sub> | 3-Ethyl-3-methylpentane    | 102.33646                               | 102.317                                   | -0.00019       |
| C <sub>8</sub> H <sub>18</sub> | 2,2,3-Trimethylpentane     | 102.38071                               | 102.370                                   | -0.00010       |
| C <sub>8</sub> H <sub>18</sub> | 2,2,4-Trimethylpentane     | 102.40902                               | 102.412                                   | 0.00003        |
| C <sub>8</sub> H <sub>18</sub> | 2,3,3-Trimethylpentane     | 102.38071                               | 102.332                                   | -0.00048       |
| C <sub>8</sub> H <sub>18</sub> | 2,3,4-Trimethylpentane     | 102.29240                               | 102.342                                   | 0.00049        |
| C <sub>8</sub> H <sub>18</sub> | 2,2,3,3-Tetramethylbutane  | 102.41632                               | 102.433                                   | 0.00016        |
| C <sub>9</sub> H <sub>20</sub> | 2,3,5-Trimethylhexane      | 114.54147                               | 114.551                                   | 0.00008        |
| C <sub>9</sub> H <sub>20</sub> | 3,3-Diethylpentane         | 114.49416                               | 114.455                                   | -0.00034       |
| C <sub>9</sub> H <sub>20</sub> | 2,2,3,3-Tetramethylpentane | 114.57402                               | 114.494                                   | -0.00070       |
| C <sub>9</sub> H <sub>20</sub> | 2,2,3,4-Tetramethylpentane | 114.51960                               | 114.492                                   | -0.00024       |

| Formula                         | Name                       | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|---------------------------------|----------------------------|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>9</sub> H <sub>20</sub>  | 2,2,4,4-Tetramethylpentane | 114.57316                               | 114.541                                   | -0.00028       |
| C <sub>9</sub> H <sub>20</sub>  | 2,3,3,4-Tetramethylpentane | 114.58266                               | 114.484                                   | -0.00086       |
| C <sub>10</sub> H <sub>22</sub> | 2-Methylnonane             | 126.64542                               | 126.680                                   | 0.00027        |
| C <sub>10</sub> H <sub>22</sub> | 5-Methylnonane             | 126.64542                               | 126.663                                   | 0.00014        |

Table 1.3. The calculated and experimental total bond energies of alkenes using closed-form equations having integers and fundamental constants only.

| Formula                         | Name                         | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|---------------------------------|------------------------------|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>3</sub> H <sub>6</sub>   | Propene                      | 35.56033                                | 35.63207                                  | 0.00201        |
| C <sub>4</sub> H <sub>8</sub>   | 1-Butene                     | 47.71803                                | 47.78477                                  | 0.00140        |
| C <sub>4</sub> H <sub>8</sub>   | trans-2-Butene               | 47.93116                                | 47.90395                                  | -0.00057       |
| C <sub>4</sub> H <sub>8</sub>   | Isobutene                    | 47.90314                                | 47.96096                                  | 0.00121        |
| C <sub>5</sub> H <sub>10</sub>  | 1-Pentene                    | 59.87573                                | 59.95094                                  | 0.00125        |
| C <sub>5</sub> H <sub>10</sub>  | trans-2-Pentene              | 60.08886                                | 60.06287                                  | -0.00043       |
| C <sub>5</sub> H <sub>10</sub>  | 2-Methyl-1-butene            | 60.06084                                | 60.09707                                  | 0.00060        |
| C <sub>5</sub> H <sub>10</sub>  | 2-Methyl-2-butene            | 60.21433                                | 60.16444                                  | -0.00083       |
| C <sub>5</sub> H <sub>10</sub>  | 3-Methyl-1-butene            | 59.97662                                | 60.01727                                  | 0.00068        |
| C <sub>6</sub> H <sub>12</sub>  | 1-Hexene                     | 72.03343                                | 72.12954                                  | 0.00133        |
| C <sub>6</sub> H <sub>12</sub>  | trans-2-Hexene               | 72.24656                                | 72.23733                                  | -0.00013       |
| C <sub>6</sub> H <sub>12</sub>  | trans-3-Hexene               | 72.24656                                | 72.24251                                  | -0.00006       |
| C <sub>6</sub> H <sub>12</sub>  | 2-Methyl-1-pentene           | 72.21854                                | 72.29433                                  | 0.00105        |
| C <sub>6</sub> H <sub>12</sub>  | 2-Methyl-2-pentene           | 72.37203                                | 72.37206                                  | 0.00000        |
| C <sub>6</sub> H <sub>12</sub>  | 3-Methyl-1-pentene           | 72.13432                                | 72.19173                                  | 0.00080        |
| C <sub>6</sub> H <sub>12</sub>  | 4-Methyl-1-pentene           | 72.10599                                | 72.21038                                  | 0.00145        |
| C <sub>6</sub> H <sub>12</sub>  | 3-Methyl-trans-2-pentene     | 72.37203                                | 72.33268                                  | -0.00054       |
| C <sub>6</sub> H <sub>12</sub>  | 4-Methyl-trans-2-pentene     | 72.34745                                | 72.31610                                  | -0.00043       |
| C <sub>6</sub> H <sub>12</sub>  | 2-Ethyl-1-butene             | 72.21854                                | 72.25909                                  | 0.00056        |
| C <sub>6</sub> H <sub>12</sub>  | 2,3-Dimethyl-1-butene        | 72.31943                                | 72.32543                                  | 0.00008        |
| C <sub>6</sub> H <sub>12</sub>  | 3,3-Dimethyl-1-butene        | 72.31796                                | 72.30366                                  | -0.00020       |
| C <sub>6</sub> H <sub>12</sub>  | 2,3-Dimethyl-2-butene        | 72.49750                                | 72.38450                                  | -0.00156       |
| C <sub>7</sub> H <sub>14</sub>  | 1-Heptene                    | 84.19113                                | 84.27084                                  | 0.00095        |
| C <sub>7</sub> H <sub>14</sub>  | 5-Methyl-1-hexene            | 84.26369                                | 84.30608                                  | 0.00050        |
| C <sub>7</sub> H <sub>14</sub>  | trans-3-Methyl-3-hexene      | 84.52973                                | 84.42112                                  | -0.00129       |
| C <sub>7</sub> H <sub>14</sub>  | 2,4-Dimethyl-1-pentene       | 84.44880                                | 84.49367                                  | 0.00053        |
| C <sub>7</sub> H <sub>14</sub>  | 4,4-Dimethyl-1-pentene       | 84.27012                                | 84.47087                                  | 0.00238        |
| C <sub>7</sub> H <sub>14</sub>  | 2,4-Dimethyl-2-pentene       | 84.63062                                | 84.54445                                  | -0.00102       |
| C <sub>7</sub> H <sub>14</sub>  | trans-4,4-Dimethyl-2-pentene | 84.54076                                | 84.54549                                  | 0.00006        |
| C <sub>7</sub> H <sub>14</sub>  | 2-Ethyl-3-methyl-1-butene    | 84.47713                                | 84.44910                                  | -0.00033       |
| C <sub>7</sub> H <sub>14</sub>  | 2,3,3-Trimethyl-1-butene     | 84.51274                                | 84.51129                                  | -0.00002       |
| C <sub>8</sub> H <sub>16</sub>  | 1-Octene                     | 96.34883                                | 96.41421                                  | 0.00068        |
| C <sub>8</sub> H <sub>16</sub>  | trans-2,2-Dimethyl-3-hexene  | 96.69846                                | 96.68782                                  | -0.00011       |
| C <sub>8</sub> H <sub>16</sub>  | 3-Ethyl-2-methyl-1-pentene   | 96.63483                                | 96.61113                                  | -0.00025       |
| C <sub>8</sub> H <sub>16</sub>  | 2,4,4-Trimethyl-1-pentene    | 96.61293                                | 96.71684                                  | 0.00107        |
| C <sub>8</sub> H <sub>16</sub>  | 2,4,4-Trimethyl-2-pentene    | 96.67590                                | 96.65880                                  | -0.00018       |
| C <sub>10</sub> H <sub>20</sub> | 1-Decene                     | 120.66423                               | 120.74240                                 | 0.00065        |
| C <sub>12</sub> H <sub>24</sub> | 1-Dodecene                   | 144.97963                               | 145.07163                                 | 0.00063        |
| C <sub>16</sub> H <sub>32</sub> | 1-Hexadecene                 | 193.61043                               | 193.71766                                 | 0.00055        |



Table 1.4. The calculated and experimental total bond energies of alkynes using closed-form equations having integers and fundamental constants only.

| Formula                        | Name     | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|--------------------------------|----------|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>3</sub> H <sub>4</sub>  | Propyne  | 29.42932                                | 29.40432                                  | -0.00085       |
| C <sub>4</sub> H <sub>6</sub>  | 1-Butyne | 41.58702                                | 41.55495                                  | -0.00077       |
| C <sub>4</sub> H <sub>6</sub>  | 2-Butyne | 41.72765                                | 41.75705                                  | 0.00070        |
| C <sub>9</sub> H <sub>16</sub> | 1-Nonyne | 102.37552                               | 102.35367                                 | -0.00021       |

Table 1.5. The calculated and experimental total bond energies of alkyl fluorides using closed-form equations having integers and fundamental constants only.

| Formula                         | Name               | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|---------------------------------|--------------------|-----------------------------------------|-------------------------------------------|----------------|
| CF <sub>4</sub>                 | Tetrafluoromethane | 21.07992                                | 21.016                                    | -0.00303       |
| CHF <sub>3</sub>                | Trifluoromethane   | 19.28398                                | 19.362                                    | 0.00405        |
| CH <sub>2</sub> F <sub>2</sub>  | Difluoromethane    | 18.22209                                | 18.280                                    | 0.00314        |
| C <sub>3</sub> H <sub>7</sub> F | 1-Fluoropropane    | 41.86745                                | 41.885                                    | 0.00041        |
| C <sub>3</sub> H <sub>7</sub> F | 2-Fluoropropane    | 41.96834                                | 41.963                                    | -0.00012       |

Table 1.6. The calculated and experimental total bond energies of alkyl chlorides using closed-form equations having integers and fundamental constants only.

| Formula                            | Name                     | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|------------------------------------|--------------------------|-----------------------------------------|-------------------------------------------|----------------|
| CCl <sub>4</sub>                   | Tetrachloromethane       | 13.43181                                | 13.448                                    | 0.00123        |
| CHCl <sub>3</sub>                  | Trichloromethane         | 14.49146                                | 14.523                                    | 0.00217        |
| CH <sub>2</sub> Cl <sub>2</sub>    | Dichloromethane          | 15.37248                                | 15.450                                    | 0.00499        |
| CH <sub>3</sub> Cl                 | Chloromethane            | 16.26302                                | 16.312                                    | 0.00299        |
| C <sub>2</sub> H <sub>5</sub> Cl   | Chloroethane             | 28.61064                                | 28.571                                    | -0.00138       |
| C <sub>3</sub> H <sub>7</sub> Cl   | 1-Chloropropane          | 40.76834                                | 40.723                                    | -0.00112       |
| C <sub>3</sub> H <sub>7</sub> Cl   | 2-Chloropropane          | 40.86923                                | 40.858                                    | -0.00028       |
| C <sub>4</sub> H <sub>9</sub> Cl   | 1-Chlorobutane           | 52.92604                                | 52.903                                    | -0.00044       |
| C <sub>4</sub> H <sub>9</sub> Cl   | 2-Chlorobutane           | 53.02693                                | 52.972                                    | -0.00104       |
| C <sub>4</sub> H <sub>9</sub> Cl   | 1-Chloro-2-methylpropane | 52.99860                                | 52.953                                    | -0.00085       |
| C <sub>4</sub> H <sub>9</sub> Cl   | 2-Chloro-2-methylpropane | 53.21057                                | 53.191                                    | -0.00037       |
| C <sub>5</sub> H <sub>11</sub> Cl  | 1-Chloropentane          | 65.08374                                | 65.061                                    | -0.00034       |
| C <sub>5</sub> H <sub>11</sub> Cl  | 1-Chloro-3-methylbutane  | 65.15630                                | 65.111                                    | -0.00069       |
| C <sub>5</sub> H <sub>11</sub> Cl  | 2-Chloro-2-methylbutane  | 65.36827                                | 65.344                                    | -0.00037       |
| C <sub>5</sub> H <sub>11</sub> Cl  | 2-Chloro-3-methylbutane  | 65.16582                                | 65.167                                    | 0.00002        |
| C <sub>6</sub> H <sub>13</sub> Cl  | 2-Chlorohexane           | 77.34233                                | 77.313                                    | -0.00038       |
| C <sub>8</sub> H <sub>17</sub> Cl  | 1-Chlorooctane           | 101.55684                               | 101.564                                   | 0.00007        |
| C <sub>12</sub> H <sub>25</sub> Cl | 1-Chlorododecane         | 150.18764                               | 150.202                                   | 0.00009        |
| C <sub>18</sub> H <sub>37</sub> Cl | 1-Chlorooctadecane       | 223.13384                               | 223.175                                   | 0.00018        |

Table 1.7. The calculated and experimental total bond energies of alkyl bromides using closed-form equations having integers and fundamental constants only.

| Formula                                        | Name                       | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|------------------------------------------------|----------------------------|-----------------------------------------|-------------------------------------------|----------------|
| CBr <sub>4</sub>                               | Tetrabromomethane          | 11.25929                                | 11.196                                    | -0.00566       |
| CHBr <sub>3</sub>                              | Tribromomethane            | 12.87698                                | 12.919                                    | 0.00323        |
| CH <sub>3</sub> Br                             | Bromomethane               | 15.67551                                | 15.732                                    | 0.00360        |
| C <sub>2</sub> H <sub>5</sub> Br               | Bromoethane                | 28.03939                                | 27.953                                    | -0.00308       |
| C <sub>3</sub> H <sub>7</sub> Br               | 1-Bromopropane             | 40.19709                                | 40.160                                    | -0.00093       |
| C <sub>3</sub> H <sub>7</sub> Br               | 2-Bromopropane             | 40.29798                                | 40.288                                    | -0.00024       |
| C <sub>3</sub> H <sub>10</sub> Br <sub>2</sub> | 2,3-Dibromo-2-methylbutane | 63.48143                                | 63.477                                    | -0.00007       |
| C <sub>6</sub> H <sub>13</sub> Br              | 1-Bromohexane              | 76.67019                                | 76.634                                    | -0.00047       |
| C <sub>7</sub> H <sub>15</sub> Br              | 1-Bromoheptane             | 88.82789                                | 88.783                                    | -0.00051       |
| C <sub>8</sub> H <sub>17</sub> Br              | 1-Bromooctane              | 100.98559                               | 100.952                                   | -0.00033       |
| C <sub>12</sub> H <sub>25</sub> Br             | 1-Bromododecane            | 149.61639                               | 149.573                                   | -0.00029       |
| C <sub>16</sub> H <sub>33</sub> Br             | 1-Bromohexadecane          | 198.24719                               | 198.192                                   | -0.00028       |

Table 1.8. The calculated and experimental total bond energies of alkyl iodides using closed-form equations having integers and fundamental constants only.

| Formula                         | Name                   | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|---------------------------------|------------------------|-----------------------------------------|-------------------------------------------|----------------|
| CHI <sub>3</sub>                | Triiodomethane         | 10.35888                                | 10.405                                    | 0.00444        |
| CH <sub>2</sub> I <sub>2</sub>  | Diiodomethane          | 12.94614                                | 12.921                                    | -0.00195       |
| CH <sub>3</sub> I               | Iodomethane            | 15.20294                                | 15.163                                    | -0.00263       |
| C <sub>2</sub> H <sub>5</sub> I | Iodoethane             | 27.36064                                | 27.343                                    | -0.00066       |
| C <sub>3</sub> H <sub>7</sub> I | 1-Iodopropane          | 39.51834                                | 39.516                                    | -0.00006       |
| C <sub>3</sub> H <sub>7</sub> I | 2-Iodopropane          | 39.61923                                | 39.623                                    | 0.00009        |
| C <sub>4</sub> H <sub>9</sub> I | 2-Iodo-2-methylpropane | 51.96057                                | 51.899                                    | -0.00119       |

Table 1.9. The calculated and experimental total bond energies of alkene halides using closed-form equations having integers and fundamental constants only.

| Formula                          | Name            | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|----------------------------------|-----------------|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>2</sub> H <sub>3</sub> Cl | Chloroethene    | 22.46700                                | 22.505                                    | 0.00170        |
| C <sub>3</sub> H <sub>3</sub> Cl | 2-Chloropropene | 35.02984                                | 35.05482                                  | 0.00071        |

Table 1.10. The calculated and experimental total bond energies of alcohols using closed-form equations having integers and fundamental constants only.

| Formula                          | Name                  | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|----------------------------------|-----------------------|-----------------------------------------|-------------------------------------------|----------------|
| CH <sub>4</sub> O                | Methanol              | 21.11038                                | 21.131                                    | 0.00097        |
| C <sub>2</sub> H <sub>6</sub> O  | Ethanol               | 33.40563                                | 33.428                                    | 0.00066        |
| C <sub>3</sub> H <sub>8</sub> O  | 1-Propanol            | 45.56333                                | 45.584                                    | 0.00046        |
| C <sub>3</sub> H <sub>8</sub> O  | 2-Propanol            | 45.72088                                | 45.766                                    | 0.00098        |
| C <sub>4</sub> H <sub>10</sub> O | 1-Butanol             | 57.72103                                | 57.736                                    | 0.00026        |
| C <sub>4</sub> H <sub>10</sub> O | 2-Butanol             | 57.87858                                | 57.922                                    | 0.00074        |
| C <sub>4</sub> H <sub>10</sub> O | 2-Methyl-1-propananol | 57.79359                                | 57.828                                    | 0.00060        |
| C <sub>4</sub> H <sub>10</sub> O | 2-Methyl-2-propananol | 58.15359                                | 58.126                                    | -0.00048       |
| C <sub>5</sub> H <sub>12</sub> O | 1-Pentanol            | 69.87873                                | 69.887                                    | 0.00011        |

| Formula                           | Name                 | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|-----------------------------------|----------------------|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>5</sub> H <sub>12</sub> O  | 2-Pentanol           | 70.03628                                | 70.057                                    | 0.00029        |
| C <sub>5</sub> H <sub>12</sub> O  | 3-Pentanol           | 70.03628                                | 70.097                                    | 0.00087        |
| C <sub>5</sub> H <sub>12</sub> O  | 2-Methyl-1-butananol | 69.95129                                | 69.957                                    | 0.00008        |
| C <sub>5</sub> H <sub>12</sub> O  | 3-Methyl-1-butananol | 69.95129                                | 69.950                                    | -0.00002       |
| C <sub>5</sub> H <sub>12</sub> O  | 2-Methyl-2-butananol | 70.31129                                | 70.246                                    | -0.00092       |
| C <sub>5</sub> H <sub>12</sub> O  | 3-Methyl-2-butananol | 69.96081                                | 70.083                                    | 0.00174        |
| C <sub>6</sub> H <sub>14</sub> O  | 1-Hexanol            | 82.03643                                | 82.054                                    | 0.00021        |
| C <sub>6</sub> H <sub>14</sub> O  | 2-Hexanol            | 82.19398                                | 82.236                                    | 0.00052        |
| C <sub>7</sub> H <sub>16</sub> O  | 1-Heptanol           | 94.19413                                | 94.214                                    | 0.00021        |
| C <sub>8</sub> H <sub>18</sub> O  | 1-Octanol            | 106.35183                               | 106.358                                   | 0.00006        |
| C <sub>8</sub> H <sub>18</sub> O  | 2-Ethyl-1-hexanol    | 106.42439                               | 106.459                                   | 0.00032        |
| C <sub>9</sub> H <sub>20</sub> O  | 1-Nonanol            | 118.50953                               | 118.521                                   | 0.00010        |
| C <sub>10</sub> H <sub>22</sub> O | 1-Decanol            | 130.66723                               | 130.676                                   | 0.00007        |
| C <sub>12</sub> H <sub>26</sub> O | 1-Dodecanol          | 154.98263                               | 154.984                                   | 0.00001        |
| C <sub>16</sub> H <sub>34</sub> O | 1-Hexadecanol        | 203.61343                               | 203.603                                   | -0.00005       |

Table 1.11. The calculated and experimental total bond energies of ethers using closed-form equations having integers and fundamental constants only.

| Formula                          | Name                    | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|----------------------------------|-------------------------|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>2</sub> H <sub>6</sub> O  | Dimethyl ether          | 32.84496                                | 32.902                                    | 0.00174        |
| C <sub>3</sub> H <sub>8</sub> O  | Ethyl methyl ether      | 45.19710                                | 45.183                                    | -0.00030       |
| C <sub>4</sub> H <sub>10</sub> O | Diethyl ether           | 57.54924                                | 57.500                                    | -0.00086       |
| C <sub>4</sub> H <sub>10</sub> O | Methyl propyl ether     | 57.35480                                | 57.355                                    | 0.00000        |
| C <sub>4</sub> H <sub>10</sub> O | Isopropyl methyl ether  | 57.45569                                | 57.499                                    | 0.00075        |
| C <sub>6</sub> H <sub>14</sub> O | Dipropyl ether          | 81.86464                                | 81.817                                    | -0.00059       |
| C <sub>6</sub> H <sub>14</sub> O | Disopropyl ether        | 82.06642                                | 82.088                                    | 0.00026        |
| C <sub>6</sub> H <sub>14</sub> O | t-Butyl ethyl ether     | 82.10276                                | 82.033                                    | -0.00085       |
| C <sub>7</sub> H <sub>16</sub> O | t-Butyl isopropyl ether | 94.36135                                | 94.438                                    | 0.00081        |
| C <sub>8</sub> H <sub>18</sub> O | Dibutyl ether           | 106.18004                               | 106.122                                   | -0.00055       |
| C <sub>8</sub> H <sub>18</sub> O | Di-sec-butyl ether      | 106.38182                               | 106.410                                   | 0.00027        |
| C <sub>8</sub> H <sub>18</sub> O | Di-t-butyl ether        | 106.36022                               | 106.425                                   | 0.00061        |
| C <sub>8</sub> H <sub>18</sub> O | t-Butyl isobutyl ether  | 106.65628                               | 106.497                                   | -0.00218       |

Table 1.12. The calculated and experimental total bond energies of 1° amines using closed-form equations having integers and fundamental constants only.

| Formula                          | Name           | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|----------------------------------|----------------|-----------------------------------------|-------------------------------------------|----------------|
| CH <sub>5</sub> N                | Methylamine    | 23.88297                                | 23.857                                    | -0.00110       |
| C <sub>2</sub> H <sub>7</sub> N  | Ethylamine     | 36.04067                                | 36.062                                    | 0.00060        |
| C <sub>3</sub> H <sub>9</sub> N  | Propylamine    | 48.19837                                | 48.243                                    | 0.00092        |
| C <sub>4</sub> H <sub>11</sub> N | Butylamine     | 60.35607                                | 60.415                                    | 0.00098        |
| C <sub>4</sub> H <sub>11</sub> N | sec-Butylamine | 60.45696                                | 60.547                                    | 0.00148        |
| C <sub>4</sub> H <sub>11</sub> N | t-Butylamine   | 60.78863                                | 60.717                                    | -0.00118       |
| C <sub>4</sub> H <sub>11</sub> N | Isobutylamine  | 60.42863                                | 60.486                                    | 0.00094        |

Table 1.13. The calculated and experimental total bond energies of 2° amines using closed-form equations having integers and fundamental constants only.

| Formula                          | Name             | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|----------------------------------|------------------|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>2</sub> H <sub>7</sub> N  | Dimethylamine    | 35.76895                                | 35.765                                    | -0.00012       |
| C <sub>4</sub> H <sub>11</sub> N | Diethylamine     | 60.22930                                | 60.211                                    | -0.00030       |
| C <sub>6</sub> H <sub>15</sub> N | Dipropylamine    | 84.54470                                | 84.558                                    | 0.00016        |
| C <sub>6</sub> H <sub>15</sub> N | Diisopropylamine | 84.74648                                | 84.846                                    | 0.00117        |
| C <sub>8</sub> H <sub>19</sub> N | Dibutylamine     | 108.86010                               | 108.872                                   | 0.00011        |
| C <sub>8</sub> H <sub>19</sub> N | Diisobutylamine  | 109.00522                               | 109.106                                   | 0.00092        |

Table 1.14. The calculated and experimental total bond energies of 3° amines using closed-form equations having integers and fundamental constants only.

| Formula                          | Name           | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|----------------------------------|----------------|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>3</sub> H <sub>9</sub> N  | Trimethylamine | 47.83338                                | 47.761                                    | -0.00152       |
| C <sub>6</sub> H <sub>15</sub> N | Triethylamine  | 84.30648                                | 84.316                                    | 0.00012        |
| C <sub>9</sub> H <sub>21</sub> N | Tripropylamine | 120.77958                               | 120.864                                   | 0.00070        |

Table 1.15. The calculated and experimental total bond energies of aldehydes using closed-form equations having integers and fundamental constants only.

| Formula                          | Name           | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|----------------------------------|----------------|-----------------------------------------|-------------------------------------------|----------------|
| CH <sub>2</sub> O                | Formaldehyde   | 15.64628                                | 15.655                                    | 0.00056        |
| C <sub>2</sub> H <sub>4</sub> O  | Acetaldehyde   | 28.18711                                | 28.198                                    | 0.00039        |
| C <sub>3</sub> H <sub>6</sub> O  | Propanal       | 40.34481                                | 40.345                                    | 0.00000        |
| C <sub>4</sub> H <sub>8</sub> O  | Butanal        | 52.50251                                | 52.491                                    | -0.00022       |
| C <sub>4</sub> H <sub>8</sub> O  | Isobutanal     | 52.60340                                | 52.604                                    | 0.00001        |
| C <sub>5</sub> H <sub>10</sub> O | Pentanal       | 64.66021                                | 64.682                                    | 0.00034        |
| C <sub>7</sub> H <sub>14</sub> O | Heptanal       | 88.97561                                | 88.942                                    | -0.00038       |
| C <sub>8</sub> H <sub>16</sub> O | Octanal        | 101.13331                               | 101.179                                   | 0.00045        |
| C <sub>8</sub> H <sub>16</sub> O | 2-Ethylhexanal | 101.20587                               | 101.259                                   | 0.00053        |

Table 1.16. The calculated and experimental total bond energies of ketones using closed-form equations having integers and fundamental constants only.

| Formula                          | Name                     | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|----------------------------------|--------------------------|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>3</sub> H <sub>6</sub> O  | Acetone                  | 40.68472                                | 40.672                                    | -0.00031       |
| C <sub>4</sub> H <sub>8</sub> O  | 2-Butanone               | 52.84242                                | 52.84                                     | -0.00005       |
| C <sub>5</sub> H <sub>10</sub> O | 2-Pentanone              | 65.00012                                | 64.997                                    | -0.00005       |
| C <sub>5</sub> H <sub>10</sub> O | 3-Pentanone              | 65.00012                                | 64.997                                    | -0.00005       |
| C <sub>5</sub> H <sub>10</sub> O | 3-Methyl-2-butanone      | 65.10101                                | 65.036                                    | -0.00099       |
| C <sub>6</sub> H <sub>12</sub> O | 2-Hexanone               | 77.15782                                | 77.152                                    | -0.00008       |
| C <sub>6</sub> H <sub>12</sub> O | 3-Hexanone               | 77.15782                                | 77.138                                    | -0.00025       |
| C <sub>6</sub> H <sub>12</sub> O | 2-Methyl-3-pentanone     | 77.25871                                | 77.225                                    | -0.00043       |
| C <sub>6</sub> H <sub>12</sub> O | 3,3-Dimethyl-2-butanone  | 77.29432                                | 77.273                                    | -0.00028       |
| C <sub>7</sub> H <sub>14</sub> O | 3-Heptanone              | 89.31552                                | 89.287                                    | -0.00032       |
| C <sub>7</sub> H <sub>14</sub> O | 4-Heptanone              | 89.31552                                | 89.299                                    | -0.00018       |
| C <sub>7</sub> H <sub>14</sub> O | 2,2-Dimethyl-3-pentanone | 89.45202                                | 89.458                                    | 0.00007        |

| Formula                          | Name                        | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|----------------------------------|-----------------------------|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>7</sub> H <sub>14</sub> O | 2,4-Dimethyl-3-pentanone    | 89.51730                                | 89.434                                    | -0.00093       |
| C <sub>8</sub> H <sub>16</sub> O | 2,2,4-Trimethyl-3-pentanone | 101.71061                               | 101.660                                   | -0.00049       |
| C <sub>9</sub> H <sub>18</sub> O | 2-Nonanone                  | 113.63092                               | 113.632                                   | 0.00001        |
| C <sub>9</sub> H <sub>18</sub> O | 5-Nonanone                  | 113.63092                               | 113.675                                   | 0.00039        |
| C <sub>9</sub> H <sub>18</sub> O | 2,6-Dimethyl-4-heptanone    | 113.77604                               | 113.807                                   | 0.00027        |

Table 1.17. The calculated and experimental total bond energies of carboxylic acids using closed-form equations having integers and fundamental constants only.

| Formula                                        | Name                       | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|------------------------------------------------|----------------------------|-----------------------------------------|-------------------------------------------|----------------|
| CH <sub>2</sub> O <sub>2</sub>                 | Formic acid                | 21.01945                                | 21.036                                    | 0.00079        |
| C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>   | Acetic acid                | 33.55916                                | 33.537                                    | -0.00066       |
| C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>   | Propanoic acid             | 45.71686                                | 45.727                                    | 0.00022        |
| C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>   | Butanoic acid              | 57.87456                                | 57.883                                    | 0.00015        |
| C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>  | Pentanoic acid             | 70.03226                                | 69.995                                    | -0.00053       |
| C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>  | 3-Methylbutanoic acid      | 70.10482                                | 70.183                                    | 0.00111        |
| C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>  | 2,2-Dimethylpropanoic acid | 70.31679                                | 69.989                                    | -0.00468       |
| C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>  | Hexanoic acid              | 82.18996                                | 82.149                                    | -0.00050       |
| C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>  | Heptanoic acid             | 94.34766                                | 94.347                                    | 0.00000        |
| C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>  | Octanoic acid              | 106.50536                               | 106.481                                   | -0.00022       |
| C <sub>9</sub> H <sub>18</sub> O <sub>2</sub>  | Nonanoic acid              | 118.66306                               | 118.666                                   | 0.00003        |
| C <sub>10</sub> H <sub>20</sub> O <sub>2</sub> | Decanoic acid              | 130.82076                               | 130.795                                   | -0.00020       |
| C <sub>12</sub> H <sub>24</sub> O <sub>2</sub> | Dodecanoic acid            | 155.13616                               | 155.176                                   | 0.00026        |
| C <sub>14</sub> H <sub>28</sub> O <sub>2</sub> | Tetradecanoic acid         | 179.45156                               | 179.605                                   | 0.00085        |
| C <sub>15</sub> H <sub>30</sub> O <sub>2</sub> | Pentadecanoic acid         | 191.60926                               | 191.606                                   | -0.00002       |
| C <sub>16</sub> H <sub>32</sub> O <sub>2</sub> | Hexadecanoic acid          | 203.76696                               | 203.948                                   | 0.00089        |
| C <sub>18</sub> H <sub>36</sub> O <sub>2</sub> | Stearic acid               | 228.08236                               | 228.298                                   | 0.00094        |
| C <sub>20</sub> H <sub>40</sub> O <sub>2</sub> | Eicosanoic acid            | 252.39776                               | 252.514                                   | 0.00046        |

Table 1.18. The calculated and experimental total bond energies of carboxylic acid esters using closed-form equations having integers and fundamental constants only.

| Formula                                        | Name                  | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|------------------------------------------------|-----------------------|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>   | Methyl formate        | 32.71076                                | 32.762                                    | 0.00156        |
| C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>   | Methyl acetate        | 45.24849                                | 45.288                                    | 0.00087        |
| C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>  | Methyl pentanoate     | 81.72159                                | 81.726                                    | 0.00005        |
| C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>  | Methyl hexanoate      | 93.87929                                | 93.891                                    | 0.00012        |
| C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>  | Methyl heptanoate     | 106.03699                               | 106.079                                   | 0.00040        |
| C <sub>9</sub> H <sub>18</sub> O <sub>2</sub>  | Methyl octanoate      | 118.19469                               | 118.217                                   | 0.00018        |
| C <sub>10</sub> H <sub>20</sub> O <sub>2</sub> | Methyl nonanoate      | 130.35239                               | 130.373                                   | 0.00016        |
| C <sub>11</sub> H <sub>22</sub> O <sub>2</sub> | Methyl decanoate      | 142.51009                               | 142.523                                   | 0.00009        |
| C <sub>12</sub> H <sub>24</sub> O <sub>2</sub> | Methyl undecanoate    | 154.66779                               | 154.677                                   | 0.00006        |
| C <sub>13</sub> H <sub>26</sub> O <sub>2</sub> | Methyl dodecanoate    | 166.82549                               | 166.842                                   | 0.00010        |
| C <sub>14</sub> H <sub>28</sub> O <sub>2</sub> | Methyl tridecanoate   | 178.98319                               | 179.000                                   | 0.00009        |
| C <sub>15</sub> H <sub>30</sub> O <sub>2</sub> | Methyl tetradecanoate | 191.14089                               | 191.170                                   | 0.00015        |
| C <sub>16</sub> H <sub>32</sub> O <sub>2</sub> | Methyl pentadecanoate | 203.29859                               | 203.356                                   | 0.00028        |
| C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>   | Propyl formate        | 57.76366                                | 57.746                                    | -0.00030       |
| C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>   | Ethyl acetate         | 57.63888                                | 57.548                                    | -0.00157       |
| C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>  | Isopropyl acetate     | 69.89747                                | 69.889                                    | -0.00013       |
| C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>  | Ethyl propanoate      | 69.79658                                | 69.700                                    | -0.00139       |
| C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>  | Butyl acetate         | 81.95428                                | 81.873                                    | -0.00099       |
| C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>  | t-Butyl acetate       | 82.23881                                | 82.197                                    | -0.00051       |

| Formula                                       | Name                          | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|-----------------------------------------------|-------------------------------|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>6</sub> H <sub>12</sub> O <sub>2</sub> | Methyl 2,2-dimethylpropanoate | 82.00612                                | 81.935                                    | -0.00087       |
| C <sub>7</sub> H <sub>14</sub> O <sub>2</sub> | Ethyl pentanoate              | 94.11198                                | 94.033                                    | -0.00084       |
| C <sub>7</sub> H <sub>14</sub> O <sub>2</sub> | Ethyl 3-methylbutanoate       | 94.18454                                | 94.252                                    | 0.00072        |
| C <sub>7</sub> H <sub>14</sub> O <sub>2</sub> | Ethyl 2,2-dimethylpropanoate  | 94.39651                                | 94.345                                    | -0.00054       |
| C <sub>8</sub> H <sub>16</sub> O <sub>2</sub> | Isobutyl isobutanoate         | 106.44313                               | 106.363                                   | -0.00075       |
| C <sub>8</sub> H <sub>16</sub> O <sub>2</sub> | Propyl pentanoate             | 106.26968                               | 106.267                                   | -0.00003       |
| C <sub>8</sub> H <sub>16</sub> O <sub>2</sub> | Isopropyl pentanoate          | 106.37057                               | 106.384                                   | 0.00013        |
| C <sub>9</sub> H <sub>18</sub> O <sub>2</sub> | Butyl pentanoate              | 118.42738                               | 118.489                                   | 0.00052        |
| C <sub>9</sub> H <sub>18</sub> O <sub>2</sub> | sec-Butyl pentanoate          | 118.52827                               | 118.624                                   | 0.00081        |
| C <sub>9</sub> H <sub>18</sub> O <sub>2</sub> | Isobutyl pentanoate           | 118.49994                               | 118.576                                   | 0.00064        |

Table 1.19. The calculated and experimental total bond energies of amides using closed-form equations having integers and fundamental constants only.

| Formula                           | Name                    | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|-----------------------------------|-------------------------|-----------------------------------------|-------------------------------------------|----------------|
| CH <sub>3</sub> NO                | Formamide               | 23.68712                                | 23.697                                    | 0.00041        |
| C <sub>2</sub> H <sub>5</sub> NO  | Acetamide               | 36.15222                                | 36.103                                    | -0.00135       |
| C <sub>3</sub> H <sub>7</sub> NO  | Propanamide             | 48.30992                                | 48.264                                    | -0.00094       |
| C <sub>4</sub> H <sub>9</sub> NO  | Butanamide              | 60.46762                                | 60.449                                    | -0.00030       |
| C <sub>4</sub> H <sub>9</sub> NO  | 2-Methylpropanamide     | 60.51509                                | 60.455                                    | -0.00099       |
| C <sub>5</sub> H <sub>11</sub> NO | Pentanamide             | 72.62532                                | 72.481                                    | -0.00200       |
| C <sub>5</sub> H <sub>11</sub> NO | 2,2-Dimethylpropanamide | 72.67890                                | 72.718                                    | 0.00054        |
| C <sub>6</sub> H <sub>13</sub> NO | Hexanamide              | 84.78302                                | 84.780                                    | -0.00004       |
| C <sub>8</sub> H <sub>17</sub> NO | Octanamide              | 109.09842                               | 109.071                                   | -0.00025       |

Table 1.20. The calculated and experimental total bond energies of N-alkyl and N,N-dialkyl amides using closed-form equations having integers and fundamental constants only.

| Formula                           | Name                  | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|-----------------------------------|-----------------------|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>3</sub> H <sub>7</sub> NO  | N,N-Dimethylformamide | 47.53142                                | 47.574                                    | 0.00090        |
| C <sub>4</sub> H <sub>9</sub> NO  | N,N-Dimethylacetamide | 59.91404                                | 59.890                                    | -0.00041       |
| C <sub>6</sub> H <sub>13</sub> NO | N-Butylacetamide      | 84.63649                                | 84.590                                    | -0.00055       |

Table 1.21. The calculated and experimental total bond energies of urea using closed-form equations having integers and fundamental constants only.

| Formula                          | Name | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|----------------------------------|------|-----------------------------------------|-------------------------------------------|----------------|
| CH <sub>4</sub> N <sub>2</sub> O | Urea | 31.35919                                | 31.393                                    | 0.00108        |

Table 1.22. The calculated and experimental total bond energies of acid halide using closed-form equations having integers and fundamental constants only.

| Formula                           | Name            | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|-----------------------------------|-----------------|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>2</sub> H <sub>3</sub> ClO | Acetyl chloride | 28.02174                                | 27.990                                    | -0.00115       |

Table 1.23. The calculated and experimental total bond energies of acid anhydrides using closed-form equations having integers and fundamental constants only.

| Formula                                       | Name                | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|-----------------------------------------------|---------------------|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>4</sub> H <sub>6</sub> O <sub>3</sub>  | Acetic anhydride    | 56.94096                                | 56.948                                    | 0.00013        |
| C <sub>6</sub> H <sub>10</sub> O <sub>3</sub> | Propanoic anhydride | 81.25636                                | 81.401                                    | 0.00177        |

Table 1.24. The calculated and experimental total bond energies of nitriles using closed-form equations having integers and fundamental constants only.

| Formula                           | Name                       | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|-----------------------------------|----------------------------|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>2</sub> H <sub>3</sub> N   | Acetonitrile               | 25.72060                                | 25.77                                     | 0.00174        |
| C <sub>3</sub> H <sub>5</sub> N   | Propanenitrile             | 37.87830                                | 37.94                                     | 0.00171        |
| C <sub>4</sub> H <sub>7</sub> N   | Butanenitrile              | 50.03600                                | 50.08                                     | 0.00082        |
| C <sub>4</sub> H <sub>7</sub> N   | 2-Methylpropanenitrile     | 50.13689                                | 50.18                                     | 0.00092        |
| C <sub>5</sub> H <sub>9</sub> N   | Pentanenitrile             | 62.19370                                | 62.26                                     | 0.00111        |
| C <sub>5</sub> H <sub>9</sub> N   | 2,2-Dimethylpropanenitrile | 62.47823                                | 62.40                                     | -0.00132       |
| C <sub>7</sub> H <sub>13</sub> N  | Heptanenitrile             | 86.50910                                | 86.59                                     | 0.00089        |
| C <sub>8</sub> H <sub>15</sub> N  | Octanenitrile              | 98.66680                                | 98.73                                     | 0.00069        |
| C <sub>10</sub> H <sub>19</sub> N | Decanenitrile              | 122.98220                               | 123.05                                    | 0.00057        |
| C <sub>14</sub> H <sub>27</sub> N | Tetradecanenitrile         | 171.61300                               | 171.70                                    | 0.00052        |

Table 1.25. The calculated and experimental total bond energies of thiols using closed-form equations having integers and fundamental constants only.

| Formula                           | Name                        | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|-----------------------------------|-----------------------------|-----------------------------------------|-------------------------------------------|----------------|
| HS                                | Hydrogen Sulfide            | 3.77430                                 | 3.653                                     | -0.03320       |
| H <sub>2</sub> S                  | Dihydrogen Sulfide          | 7.56058                                 | 7.605                                     | 0.00582        |
| CH <sub>4</sub> S                 | Methanethiol                | 19.60264                                | 19.575                                    | -0.00141       |
| C <sub>2</sub> H <sub>6</sub> S   | Ethanethiol                 | 31.76034                                | 31.762                                    | 0.00005        |
| C <sub>3</sub> H <sub>8</sub> S   | 1-Propanethiol              | 43.91804                                | 43.933                                    | 0.00035        |
| C <sub>3</sub> H <sub>8</sub> S   | 2-Propanethiol              | 44.01893                                | 44.020                                    | 0.00003        |
| C <sub>4</sub> H <sub>10</sub> S  | 1-Butanethiol               | 56.07574                                | 56.089                                    | 0.00024        |
| C <sub>4</sub> H <sub>10</sub> S  | 2-Butanethiol               | 56.17663                                | 56.181                                    | 0.00009        |
| C <sub>4</sub> H <sub>10</sub> S  | 2-Methyl-1-propanethiol     | 56.14830                                | 56.186                                    | 0.00066        |
| C <sub>4</sub> H <sub>10</sub> S  | 2-Methyl-2-propanethiol     | 56.36027                                | 56.313                                    | -0.00084       |
| C <sub>5</sub> H <sub>12</sub> S  | 2-Methyl-1-butanethiol      | 68.30600                                | 68.314                                    | 0.00012        |
| C <sub>5</sub> H <sub>12</sub> S  | 1-Pentanethiol              | 68.23344                                | 68.264                                    | 0.00044        |
| C <sub>5</sub> H <sub>12</sub> S  | 2-Methyl-2-butanethiol      | 68.51797                                | 68.441                                    | -0.00113       |
| C <sub>5</sub> H <sub>12</sub> S  | 3-Methyl-2-butanethiol      | 68.31552                                | 68.381                                    | 0.00095        |
| C <sub>5</sub> H <sub>12</sub> S  | 2,2-Dimethyl-1-propanethiol | 68.51797                                | 68.461                                    | -0.00084       |
| C <sub>6</sub> H <sub>14</sub> S  | 1-Hexanethiol               | 80.39114                                | 80.416                                    | 0.00031        |
| C <sub>6</sub> H <sub>14</sub> S  | 2-Methyl-2-pentanethiol     | 80.67567                                | 80.607                                    | -0.00085       |
| C <sub>6</sub> H <sub>14</sub> S  | 2,3-Dimethyl-2-butanethiol  | 80.71992                                | 80.603                                    | -0.00145       |
| C <sub>7</sub> H <sub>16</sub> S  | 1-Heptanethiol              | 92.54884                                | 92.570                                    | 0.00023        |
| C <sub>10</sub> H <sub>22</sub> S | 1-Decanethiol               | 129.02194                               | 129.048                                   | 0.00020        |

Table 1.26. The calculated and experimental total bond energies of sulfides using closed-form equations having integers and fundamental constants only.

| Formula                           | Name                     | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|-----------------------------------|--------------------------|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>2</sub> H <sub>6</sub> S   | Dimethyl sulfide         | 31.65668                                | 31.672                                    | 0.00048        |
| C <sub>3</sub> H <sub>8</sub> S   | Ethyl methyl sulfide     | 43.81438                                | 43.848                                    | 0.00078        |
| C <sub>4</sub> H <sub>10</sub> S  | Diethyl sulfide          | 55.97208                                | 56.043                                    | 0.00126        |
| C <sub>4</sub> H <sub>10</sub> S  | Methyl propyl sulfide    | 55.97208                                | 56.029                                    | 0.00102        |
| C <sub>4</sub> H <sub>10</sub> S  | Isopropyl methyl sulfide | 56.07297                                | 56.115                                    | 0.00075        |
| C <sub>5</sub> H <sub>12</sub> S  | Butyl methyl sulfide     | 68.12978                                | 68.185                                    | 0.00081        |
| C <sub>5</sub> H <sub>12</sub> S  | t-Butyl methyl sulfide   | 68.28245                                | 68.381                                    | 0.00144        |
| C <sub>5</sub> H <sub>12</sub> S  | Ethyl propyl sulfide     | 68.12978                                | 68.210                                    | 0.00117        |
| C <sub>5</sub> H <sub>12</sub> S  | Ethyl isopropyl sulfide  | 68.23067                                | 68.350                                    | 0.00174        |
| C <sub>6</sub> H <sub>14</sub> S  | Diisopropyl sulfide      | 80.48926                                | 80.542                                    | 0.00065        |
| C <sub>6</sub> H <sub>14</sub> S  | Butyl ethyl sulfide      | 80.28748                                | 80.395                                    | 0.00133        |
| C <sub>6</sub> H <sub>14</sub> S  | Methyl pentyl sulfide    | 80.28748                                | 80.332                                    | 0.00056        |
| C <sub>8</sub> H <sub>18</sub> S  | Dibutyl sulfide          | 104.60288                               | 104.701                                   | 0.00094        |
| C <sub>8</sub> H <sub>18</sub> S  | Di-sec-butyl sulfide     | 104.80466                               | 104.701                                   | -0.00099       |
| C <sub>8</sub> H <sub>18</sub> S  | Di-t-butyl sulfide       | 104.90822                               | 104.920                                   | 0.00011        |
| C <sub>8</sub> H <sub>18</sub> S  | Diisobutyl sulfide       | 104.74800                               | 104.834                                   | 0.00082        |
| C <sub>10</sub> H <sub>22</sub> S | Ethyl propyl sulfide     | 128.91828                               | 128.979                                   | 0.00047        |
| C <sub>10</sub> H <sub>22</sub> S | Diisopentyl sulfide      | 129.06340                               | 129.151                                   | 0.00068        |

Table 1.27. The calculated and experimental total bond energies of disulfides using closed-form equations having integers and fundamental constants only.

| Formula                                       | Name                 | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|-----------------------------------------------|----------------------|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>2</sub> H <sub>6</sub> S <sub>2</sub>  | Dimethyl disulfide   | 34.48127                                | 34.413                                    | -0.00199       |
| C <sub>4</sub> H <sub>10</sub> S <sub>2</sub> | Diethyl disulfide    | 58.79667                                | 58.873                                    | 0.00129        |
| C <sub>6</sub> H <sub>14</sub> S <sub>2</sub> | Dipropyl disulfide   | 83.11207                                | 83.169                                    | 0.00068        |
| C <sub>8</sub> H <sub>18</sub> S <sub>2</sub> | Di-t-butyl disulfide | 107.99653                               | 107.919                                   | -0.00072       |

Table 1.28. The calculated and experimental total bond energies of sulfoxides using closed-form equations having integers and fundamental constants only.

| Formula                           | Name               | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|-----------------------------------|--------------------|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>2</sub> H <sub>6</sub> SO  | Dimethyl sulfoxide | 35.52450                                | 35.435                                    | -0.00253       |
| C <sub>4</sub> H <sub>10</sub> SO | Diethyl sulfoxide  | 59.83990                                | 59.891                                    | 0.00085        |
| C <sub>6</sub> H <sub>14</sub> SO | Dipropyl sulfoxide | 84.15530                                | 84.294                                    | 0.00165        |

Table 1.29. The calculated and experimental total bond energies of sulfones using closed-form equations having integers and fundamental constants only.

| Formula                                       | Name             | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|-----------------------------------------------|------------------|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>2</sub> H <sub>6</sub> SO <sub>2</sub> | Dimethyl sulfone | 40.27588                                | 40.316                                    | 0.00100        |



Table 1.30. The calculated and experimental total bond energies of sulfites using closed-form equations having integers and fundamental constants only.

| Formula                                        | Name             | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|------------------------------------------------|------------------|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>2</sub> H <sub>6</sub> SO <sub>3</sub>  | Dimethyl sulfite | 43.95058                                | 44.042                                    | 0.00207        |
| C <sub>4</sub> H <sub>10</sub> SO <sub>3</sub> | Diethyl sulfite  | 68.54939                                | 68.648                                    | 0.00143        |
| C <sub>8</sub> H <sub>18</sub> SO <sub>3</sub> | Dibutyl sulfite  | 117.18019                               | 117.191                                   | 0.00009        |

Table 1.31. The calculated and experimental total bond energies of sulfates using closed-form equations having integers and fundamental constants only.

| Formula                                        | Name             | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|------------------------------------------------|------------------|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>2</sub> H <sub>6</sub> SO <sub>4</sub>  | Dimethyl sulfate | 48.70617                                | 48.734                                    | 0.00058        |
| C <sub>4</sub> H <sub>10</sub> SO <sub>4</sub> | Diethyl sulfate  | 73.30077                                | 73.346                                    | 0.00061        |
| C <sub>6</sub> H <sub>14</sub> SO <sub>4</sub> | Dipropyl sulfate | 97.61617                                | 97.609                                    | -0.00008       |

Table 1.32. The calculated and experimental total bond energies of nitro alkanes using closed-form equations having integers and fundamental constants only.

| Formula                                        | Name             | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|------------------------------------------------|------------------|-----------------------------------------|-------------------------------------------|----------------|
| CH <sub>3</sub> NO <sub>2</sub>                | Nitromethane     | 25.14934                                | 25.107                                    | -0.00168       |
| C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub>  | Nitroethane      | 37.30704                                | 37.292                                    | -0.00040       |
| C <sub>3</sub> H <sub>7</sub> NO <sub>2</sub>  | 1-Nitropropane   | 49.46474                                | 49.451                                    | -0.00028       |
| C <sub>3</sub> H <sub>7</sub> NO <sub>2</sub>  | 2-Nitropropane   | 49.56563                                | 49.602                                    | 0.00074        |
| C <sub>4</sub> H <sub>9</sub> NO <sub>2</sub>  | 1-Nitrobutane    | 61.62244                                | 61.601                                    | -0.00036       |
| C <sub>4</sub> H <sub>9</sub> NO <sub>2</sub>  | 2-Nitroisobutane | 61.90697                                | 61.945                                    | 0.00061        |
| C <sub>5</sub> H <sub>11</sub> NO <sub>2</sub> | 1-Nitropentane   | 73.78014                                | 73.759                                    | -0.00028       |

Table 1.33. The calculated and experimental total bond energies of nitrite using closed-form equations having integers and fundamental constants only.

| Formula                         | Name           | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|---------------------------------|----------------|-----------------------------------------|-------------------------------------------|----------------|
| CH <sub>3</sub> NO <sub>2</sub> | Methyl nitrite | 24.92328                                | 24.955                                    | 0.00126        |

Table 1.34. The calculated and experimental total bond energies of nitrate using closed-form equations having integers and fundamental constants only.

| Formula                                       | Name              | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|-----------------------------------------------|-------------------|-----------------------------------------|-------------------------------------------|----------------|
| CH <sub>3</sub> NO <sub>3</sub>               | Methyl nitrate    | 28.18536                                | 28.117                                    | -0.00244       |
| C <sub>2</sub> H <sub>5</sub> NO <sub>3</sub> | Ethyl nitrate     | 40.34306                                | 40.396                                    | 0.00131        |
| C <sub>3</sub> H <sub>7</sub> NO <sub>3</sub> | Propyl nitrate    | 52.50076                                | 52.550                                    | 0.00093        |
| C <sub>3</sub> H <sub>7</sub> NO <sub>3</sub> | Isopropyl nitrate | 52.60165                                | 52.725                                    | 0.00233        |

Table 1.35. The calculated and experimental total bond energies of conjugated alkenes using closed-form equations having integers and fundamental constants only.

| Formula                       | Name                | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|-------------------------------|---------------------|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>5</sub> H <sub>8</sub> | Cyclopentene        | 54.83565                                | 54.86117                                  | 0.00047        |
| C <sub>4</sub> H <sub>6</sub> | 1,3 Butadiene       | 42.09159                                | 42.12705                                  | 0.00084        |
| C <sub>5</sub> H <sub>8</sub> | 1,3 Pentadiene      | 54.40776                                | 54.42484                                  | 0.00031        |
| C <sub>5</sub> H <sub>8</sub> | 1,4 Pentadiene      | 54.03745                                | 54.11806                                  | 0.00149        |
| C <sub>5</sub> H <sub>6</sub> | 1,3 Cyclopentadiene | 49.27432                                | 49.30294                                  | 0.00058        |

Table 1.36. The calculated and experimental total bond energies of aromatics and heterocyclic aromatics using closed-form equations having integers and fundamental constants only.

| Formula                                                     | Name                      | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|-------------------------------------------------------------|---------------------------|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>6</sub> H <sub>6</sub>                               | Benzene                   | 57.26008                                | 57.26340                                  | 0.00006        |
| C <sub>6</sub> H <sub>5</sub> Cl                            | Chlorobenzene             | 56.55263                                | 56.581                                    | 0.00051        |
| C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>               | m-dichlorobenzene         | 55.84518                                | 55.852                                    | 0.00012        |
| C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub>               | 1,2,3-trichlorobenzene    | 55.13773                                | 55.077                                    | -0.00111       |
| C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub>               | 1,3,5-trichlorobenzene    | 55.29542                                | 55.255                                    | -0.00073       |
| C <sub>6</sub> Cl <sub>6</sub>                              | Hexachlorobenzene         | 52.57130                                | 52.477                                    | -0.00179       |
| C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>               | Nitrobenzene              | 65.18754                                | 65.217                                    | 0.00046        |
| C <sub>7</sub> H <sub>8</sub>                               | Toluene                   | 69.48425                                | 69.546                                    | 0.00088        |
| C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>                | Benzoic acid              | 73.76938                                | 73.762                                    | -0.00009       |
| C <sub>7</sub> H <sub>5</sub> ClO <sub>2</sub>              | 2-chlorobenzoic acid      | 73.06193                                | 73.082                                    | 0.00027        |
| C <sub>7</sub> H <sub>5</sub> ClO <sub>2</sub>              | 3-chlorobenzoic acid      | 73.26820                                | 73.261                                    | -0.00010       |
| C <sub>7</sub> H <sub>5</sub> ClO <sub>2</sub>              | 4-chlorobenzoic acid      | 73.26820                                | 73.247                                    | -0.00028       |
| C <sub>6</sub> H <sub>7</sub> N                             | Aniline                   | 64.43373                                | 64.374                                    | -0.00093       |
| C <sub>7</sub> H <sub>9</sub> N                             | 2-methylaniline           | 76.62345                                | 76.643                                    | -0.00025       |
| C <sub>7</sub> H <sub>9</sub> N                             | 3-methylaniline           | 76.62345                                | 76.661                                    | 0.00050        |
| C <sub>7</sub> H <sub>9</sub> N                             | 4-methylaniline           | 76.62345                                | 76.654                                    | 0.00040        |
| C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub> | 2-nitroaniline            | 72.47476                                | 72.424                                    | -0.00070       |
| C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub> | 3-nitroaniline            | 72.47476                                | 72.481                                    | -0.00009       |
| C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub> | 4-nitroaniline            | 72.47476                                | 72.476                                    | -0.00002       |
| C <sub>7</sub> H <sub>7</sub> NO <sub>2</sub>               | Aniline-2-carboxylic acid | 80.90857                                | 80.941                                    | 0.00041        |
| C <sub>7</sub> H <sub>7</sub> NO <sub>2</sub>               | Aniline-3-carboxylic acid | 80.90857                                | 80.813                                    | -0.00118       |
| C <sub>7</sub> H <sub>7</sub> NO <sub>2</sub>               | Aniline-4-carboxylic acid | 80.90857                                | 80.949                                    | 0.00050        |
| C <sub>6</sub> H <sub>6</sub> O                             | Phenol                    | 61.75817                                | 61.704                                    | -0.00087       |
| C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> O <sub>5</sub> | 2,4-dinitrophenol         | 77.61308                                | 77.642                                    | 0.00037        |
| C <sub>6</sub> H <sub>8</sub> O                             | Anisole                   | 73.39006                                | 73.355                                    | -0.00047       |
| C <sub>10</sub> H <sub>8</sub>                              | Naphthalene               | 90.74658                                | 90.79143                                  | 0.00049        |
| C <sub>4</sub> H <sub>5</sub> N                             | Pyrrole                   | 44.81090                                | 44.785                                    | -0.00057       |
| C <sub>4</sub> H <sub>4</sub> O                             | Furan                     | 41.67782                                | 41.692                                    | 0.00033        |
| C <sub>4</sub> H <sub>4</sub> S                             | Thiophene                 | 40.42501                                | 40.430                                    | 0.00013        |
| C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>                | Imidazole                 | 39.76343                                | 39.74106                                  | -0.00056       |
| C <sub>5</sub> H <sub>5</sub> N                             | Pyridine                  | 51.91802                                | 51.87927                                  | -0.00075       |
| C <sub>4</sub> H <sub>4</sub> N <sub>2</sub>                | Pyrimidine                | 46.57597                                | 46.51794                                  | -0.00125       |
| C <sub>4</sub> H <sub>4</sub> N <sub>2</sub>                | Pyrazine                  | 46.57597                                | 46.51380                                  | 0.00095        |
| C <sub>9</sub> H <sub>7</sub> N                             | Quinoline                 | 85.40453                                | 85.48607                                  | 0.00178        |
| C <sub>9</sub> H <sub>7</sub> N                             | Isoquinoline              | 85.40453                                | 85.44358                                  | 0.00046        |
| C <sub>8</sub> H <sub>7</sub> N                             | Indole                    | 78.52215                                | 78.514                                    | -0.00010       |
| C <sub>5</sub> H <sub>5</sub> N <sub>5</sub>                | Adenine                   | 70.83735                                | 70.79811                                  | -0.00055       |

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## Section V1

## Software Program

The present invention relates to a system of computing and rendering the nature of at least one specie selected from a group of diatomic molecules having at least one atom that is other than hydrogen, polyatomic molecules, molecular ions, polyatomic molecular ions, or molecular radicals, or any functional group therein, comprising physical, Maxwellian solutions of charge, mass, and current density functions of said specie, said system comprising: processing means for processing physical, Maxwellian equations representing charge, mass, and current density functions of said specie; and an output device in communication with the processing means for displaying said physical, Maxwellian solutions of charge, mass, and current density functions of said specie.

In one embodiment, for example, the system comprises five components: (1) the graphical user interface (GUI); (2) the routine for parsing between an input chemical structure or name and taking the input and activating a routine to call up the parts of the molecule (functional groups), which are used for determining the energies and structure to be rendered; (3) the functional-group data base that has an organization of the theoretical solutions; (4) the rendering engine, which calculates and enables manipulations of the image, such as a three-dimensional model in response to commands, as well as responds to commands for data parameters corresponding to the image such as bond energies and charge distribution and geometrical parameters; and (5) data transfer system for inputting numerical data into or out of the computational components and storage components of the main system. The system further comprises spreadsheets with solutions of the bond parameters with output in any standard spreadsheet format. The system also comprises a data-handling program to transfer data from the spreadsheets into the main program.

The output may be, for example, at least one of graphical, simulation, text, and numerical data. The output may be the calculation of at least one of: (1) a bond distance between two atoms; (2) a bond angle between three of the atoms; (3) a bond energy between two atoms; (4) orbital intercept distances and angles; and (5) charge-density functions of atomic, hybridized, and molecular orbitals, wherein the bond distance, bond angle, and bond energy are calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration.



In other embodiments, the charge, current, energy, and geometrical parameters are output to be inputs to other programs that may be used in further applications. For example, the data of heats of formation may be input to another program to be used to predict stability (existence of compounds) equilibrium constants and to predict synthetic pathways. That is, a novel composition of matter may be discovered by calculating at least one of a bond distance between two of the atoms, a bond angle between three of the atoms, and a bond energy between two of the atoms, orbital intercept distances and angles, charge-density functions of atomic, hybridized, and molecular orbitals, the bond distance, bond angle, and bond energy being calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration. The charge and current density functions may be used to predict the electric and magnetic fields of the species to determine other properties due to the interaction of the fields between species. These fields and the predictions of field interactions may be computed using Maxwell's equations. In one embodiment, finite-element analysis is used to predict or calculate the interaction and resulting properties, such as the freezing point, boiling point, density, viscosity, and refractive index. Furthermore, the output data can be used to give thermodynamic, spectroscopic, and other properties, aid in drug design and other applications with or without direct visualization. Furthermore, the data can be input into other programs of the system, which calculate thermodynamic and other properties, or performs a simulation, such as a chemical reaction or molecular dynamics.

The output data may be used to predict a composition of matter comprising a plurality of atoms, the improvement comprising a novel property or use discovered by calculation of at least one of a bond distance between two of the atoms, a bond angle between three of the atoms, and a bond energy between two of the atoms, orbital intercept distances and angles, charge-density functions of atomic, hybridized, and molecular orbitals, the bond distance, bond angle, and bond energy being calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration. The novel property, for example, may be a new pharmaceutical use, or stability at room temperature of a novel arrangement of atoms or ions.

In one embodiment, the output device of the system is a display that displays at least one of visual or graphical media. The display may be at least one of static or dynamic. At least one of vibration, rotation, and translation may be displayed. The displayed information

may be used for at least one of modeling reactivity, predicting physical properties, and aiding in drug and material design. The output device may be a monitor, video projector, printer, or one-, two- or three-dimensional rendering device. The displayed information may be used to model other molecules and provides utility to anticipate their reactivity and physical properties.

5 Additionally, data may be output and used in the same and additional applications as the rendered models and representations of the calculated physical solutions. The processing means of the system may be a general-purpose computer. The general-purpose computer may comprise a central processing unit (CPU), one or more specialized processors, system memory, a mass storage device such as a magnetic disk, an optical disk, or other storage device, an input  
10 means. The input means may comprise a serial port, USB port, microphone input, camera input, keyboard or mouse. The processing means comprises a special purpose computer or other hardware system. The system may comprise computer program products such as computer readable medium having embodied therein program code means. The computer readable media may be any available media which can be accessed by a general purpose or  
15 special purpose computer. The computer readable media may comprise, for example, at least one of RAM, ROM, EPROM, CD ROM, DVD or other optical disk storage, magnetic disk storage or other magnetic storage devices, or any other medium that can embody the desired program code means and which can be accessed by a general purpose or special purpose computer. The program code means may comprise executable instructions and data, which  
20 cause a general purpose computer or special purpose computer to perform a certain function of a group of functions. Commercial examples of suitable program language includes, for example, C++, C, JAVA, FORTRAN, Python and Assembly Languages, programmed with an algorithm based on the physical solutions, and the computer may be a PC, mainframe, supercomputer, or cluster of computers. Commercial examples of suitable programs include,  
25 for example, APIs like OpenGL, DirectX, FOX GUI toolkit, and Qt. This program may be developed to run on at least one of operating systems like Windows XP, Windows 2000, Windows Vista, MAC OS, MAC OS X, Linux, Unix, Irix and other Unix-type operating systems.

Millsian software is designed to render 3-D models of molecules, molecular ions,  
30 molecular radicals, functional groups thereof, and related structure and property information and produce useful data output and application of the parameters of these species, wherein the nature of their bound electrons and chemical bonds are solved using Dr. Randell L. Mills' Classical Quantum Mechanics theory described in the reference: R. L. Mills, "The Grand Unified Theory of Classical Quantum Mechanics", June 2006 Edition, Cadmus Professional

Communications-Science Press Division, Ephrata, PA, ISBN 0963517171, Library of Congress Control Number 2005936834; posted at

<http://www.blacklightpower.com/bookdownload.shtml>, which is incorporated by this reference in its entirety. Figure 76 provides a flow chart diagram, which is an example of a software

5 system that can be utilized for this purpose, which example is not intended to limit the scope of the disclosed inventions. The main parts of this exemplary software system illustrated in Figure 76 will now be further explained:

Start: A user can start the program by running an executable program file. That might  
10 be done, for example, by double clicking the program icon on a Windows-based operating system, or typing the name of the executable file on the command line and pressing the 'Enter' key on a Linux or Unix operating system. The program initially starts by reading data files located in specific directories. The names of those directories and locations are fixed according to the type and format of the data files.

15 Data files: There are two types of data files used in the software system: functional group data files and molecule data files. Functional group data files contain information about various functional groups. Functional groups are the basic bonding elements or units that each typically comprise an atom, or at least two atoms bound together as found within a molecule (e.g. -Cl, C=C, C=O, CH<sub>3</sub>). Functional groups typically dictate or define properties and  
20 structure of the molecule. Similar functional groups in different molecules typically react in similar ways when subjected to a particular set of reaction conditions. Molecule data files contain information about molecules, molecular ions, and molecular radicals. These data files are processed according to their file formats.

File formats: Millsian software employs two kinds of file formats for storing  
25 information about the structure, energies and names of molecules and functional groups: raw-data format and hierarchical format. In a raw-data file, all information is stored as is, below the header describing the type of information. As shown in the Table below, for example, the names of the molecule or functional group are listed below the #NAMES header. The names and positions of the atoms are listed below the #ATOMS header, and so on.

```

#NAMES
CH3
Alkane CH3

#SMILES
C-

#ATOMS
1      C      0      0      0
2      H      1.9775 -0.698 0
3      H      -0.9888      -0.698 1.712
4      H      -0.9888      -0.698 -1.712

#AO
1      1 1s    0.171 2
2      1 2sp3  0.864 -1

#BONDS
1      1 2      1      1.649
2      1 3      1      1.649
3      1 4      1      1.649

#BONDAXES
1      1      1      90      0      0

#DATA
RCH bond angle: 109.44°
CH bond length: 2.097 a
HFORM: 12.492

```

Most of the functional groups files and some simple molecule files are stored in raw data format. The other file format used with the Millsian software system, the hierarchical file format, represents the information in a graph style, in which nodes are connected to other nodes through links. This format is designed to construct molecules by attaching different functional groups in a desired manner. Using this file format, the user can construct complex molecules built from solved functional groups.

For example, as shown in the Table below, the pentane data file includes a #GROUPS header below which is list all of the functional groups that form a part of the pentane molecule. Under the #GROUP\_LINKS header is information about how these functional groups are connected to each other to construct pentane.

```
#NAMES
Pentane

#SMILES
CCCCC

#GROUPS
1      C-
2      -C-
3      -C-
4      -C-
5      C-

#GROUP_LINKS
1      1 1      2 1      180
2      2 2      3 1      180
3      3 2      4 1      180
4      4 2      5 1      180
```

Processing data files: As further shown in the flow diagram of Figure 76 for the exemplary Millsian software system, the program first processes the functional group data file and constructs the functional-group objects, which are complete 3-D representations of the functional groups and their related information supplied in the corresponding file. These objects are then ready to be visually displayed through use of a molecule viewer. Next, the program processes the molecule data file. If the molecule data file is in raw-data format, then the program makes a molecule object directly from it. If the file is in hierarchical format, then the program calculates geometric parameters from listed functional groups. The program stores all functional-group objects and molecule objects using internal data structures.

Visualization/ User Interactions: As shown in Figures 77 and 78, the molecule viewer displays the functional-group objects and molecule objects and provides basic interaction capabilities with the displayed objects, such as rotating, scaling, and moving the objects. The molecule viewer also provides other visualization options, such as viewing molecules in wire frame mode, viewing coordinate axes, and changing of the transparency and lighting. The user, for example, can also select parts of a molecule for visualization, like a nucleus, atomic orbital, molecular orbital, or bond axis. The viewer also includes a drop down information window, which provides, for example, related information about molecules, such as bond angles, component functional groups, and total heat of formation. In one embodiment, a user can create new molecules by joining functional groups. For this purpose, the user can select a

first functional group. Next, the user can select an open bond from the functional group where the user desires to attach another group. Next, the user can select another or the same functional group, followed by selecting an open bond from the other group. The user can join the two selected functional groups at the selected open bonds by clicking on 'Join Groups'.

- 5 This method of joining functional groups at open bonds can be repeated to form the desired molecule.

SMILES input: The Simplified Molecular Input Line Entry Specification or SMILES is a specification for unambiguously describing the structure of chemical molecules using short ASCII strings. Through the user interface, a user can enter SMILES to construct molecules,

- 10 provided the new molecule comprises functional groups that are in the database. Once a SMILES is entered, a parser reads in and breaks it down into component functional groups. The software system then attaches the component functional groups to create the new molecule object, which can then be viewed using the molecule viewer.

- While the claimed invention has been described in detail and with reference to specific  
15 embodiments thereof, it will be apparent to one of ordinary skill in the art that various changes and modifications can be made to the claimed invention without departing from the spirit and scope thereof.

CONTINUOUS-CHAIN ALKANES ( $C_nH_{2n+2}$ ,  $n = 3, 4, 5 \dots \infty$ )

The continuous-chain alkanes,  $C_nH_{2n+2}$ , are the homologous series comprising terminal methyl groups at each end of the chain with  $n - 2$  methylene ( $CH_2$ ) groups in between:



5  $C_nH_{2n+2}$  can be solved using the same principles as those used to solve ethane and ethylene wherein the  $2s$  and  $2p$  shells of each  $C$  hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Three  $H$  AOs combine with three carbon  $2sp^3$  HOs and two  $H$  AOs combine with  
 10 two carbon  $2sp^3$  HOs to form each methyl and methylene group, respectively, where each bond comprises a  $H_2$ -type MO developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section. The  $CH_3$  and  $CH_2$  groups bond by forming  $H_2$ -type MOs between the remaining  $C2sp^3$  HOs on the carbons such that each carbon forms four bonds involving its four  $C2sp^3$  HOs. For the alkyl  $C-C$  group,  $E_T(atom-atom,msp^3.AO)$  is  
 15  $-1.85836 \text{ eV}$  where both energy contributions are given by Eq. (14.513). It is based on the energy match between the  $C2sp^3$  HOs of the chain comprising methylene groups and terminal methyl groups.

The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of straight-chain alkanes are given in Tables 15.4,  
 20 15.5, and 15.6, respectively. The total energy of each straight-chain alkane given in Table 15.7 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.6 corresponding to functional-group composition of the molecule. The bond angle parameters of straight-chain alkanes determined using Eqs. (15.79-15.108) are given in Table 15.8. In this angle table and those given in subsequent sections when  $c'_2$  is given as the ratio of two values of  
 25  $c_2$  designated to Atom 1 and Atom 2 and corresponding to  $E_{Coulombic}$  of Atom 1 and Atom 2,

$$\text{respectively, then } c'_2 = \frac{c_2(Atom\ 2)}{c_2(Atom\ 1)}.$$

Table 15.4. The geometrical bond parameters of straight-chain alkanes and experimental values [1].

| Parameter                | C'-C'<br>Group                          | C'-H (CH <sub>3</sub> )<br>Group                | C'-H (CH <sub>2</sub> )<br>Group                |
|--------------------------|-----------------------------------------|-------------------------------------------------|-------------------------------------------------|
| $a$ (a <sub>0</sub> )    | 2.12499                                 | 1.64920                                         | 1.67122                                         |
| $c'$ (a <sub>0</sub> )   | 1.45744                                 | 1.04856                                         | 1.05553                                         |
| Bond Length<br>2c' (Å)   | 1.54280                                 | 1.10974                                         | 1.11713                                         |
| Exp. Bond Length<br>(Å)  | 1.532<br>(propane)<br>1.531<br>(butane) | 1.107<br>(C-H propane)<br>1.117<br>(C-H butane) | 1.107<br>(C-H propane)<br>1.117<br>(C-H butane) |
| $h, c$ (a <sub>0</sub> ) | 1.54616                                 | 1.27295                                         | 1.29569                                         |
| $\sigma$                 | 0.68600                                 | 0.63580                                         | 0.63159                                         |

Table 15.5. The MO to HO intercept geometrical bond parameters of straight-chain alkanes.  $E_r$  is  $E_r(atom - atom, nsp^3, AC)$ .

| Bond                                                           | Atom           | $E_r$<br>(eV)<br>Bond 1 | $E_r$<br>(eV)<br>Bond 2 | $E_r$<br>(eV)<br>Bond 3 | $E_r$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>C2sp <sup>3</sup><br>(eV) | $r_{final}$<br>(a <sub>0</sub> ) | $r_{bond}$<br>(a <sub>0</sub> ) | $E_{r_{intercept}}$<br>(eV)<br>Final | $E(C2sp^3)$<br>(eV)<br>Final | $\theta'$<br>(°) | $\theta_1$<br>(°) | $\theta_2$<br>(°) | $d_1$<br>(a <sub>0</sub> ) | $d_2$<br>(a <sub>0</sub> ) |
|----------------------------------------------------------------|----------------|-------------------------|-------------------------|-------------------------|-------------------------|----------------------------------------------------|----------------------------------|---------------------------------|--------------------------------------|------------------------------|------------------|-------------------|-------------------|----------------------------|----------------------------|
| C-H (CH <sub>3</sub> )                                         | C              | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                         | 0.91771                          | 0.86359                         | -15.75493                            | -15.56407                    | 77.49            | 102.51            | 41.48             | 1.23564                    | 0.18703                    |
| C-H (CH <sub>2</sub> )                                         | C              | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                         | 0.91771                          | 0.81549                         | -16.68412                            | -16.49325                    | 68.47            | 111.53            | 35.84             | 1.35486                    | 0.29933                    |
| H <sub>3</sub> C-C <sub>2</sub> H <sub>4</sub> CH <sub>3</sub> | C <sub>2</sub> | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                         | 0.91771                          | 0.86359                         | -15.75493                            | -15.56407                    | 63.82            | 116.18            | 30.08             | 1.83879                    | 0.38106                    |
| H <sub>3</sub> C-C <sub>2</sub> H <sub>4</sub> CH <sub>2</sub> | C <sub>3</sub> | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                         | 0.91771                          | 0.81549                         | -16.68412                            | -16.49325                    | 56.41            | 123.59            | 26.06             | 1.90890                    | 0.45117                    |



Table 15.6. The energy parameters (eV) of functional groups of straight-chain alkanes.

| Parameters                        | C – C<br>Group | CH <sub>3</sub><br>Group  | CH <sub>2</sub><br>Group  |
|-----------------------------------|----------------|---------------------------|---------------------------|
| $n_1$                             | 1              | 3                         | 2                         |
| $n_2$                             | 0              | 2                         | 1                         |
| $n_3$                             | 0              | 0                         | 0                         |
| $C_1$                             | 0.5            | 0.75                      | 0.75                      |
| $C_2$                             | 1              | 1                         | 1                         |
| $c_1$                             | 1              | 1                         | 1                         |
| $c_2$                             | 0.91771        | 0.91771                   | 0.91771                   |
| $c_3$                             | 0              | 0                         | 1                         |
| $c_4$                             | 2              | 1                         | 1                         |
| $c_5$                             | 0              | 3                         | 2                         |
| $C_{1o}$                          | 0.5            | 0.75                      | 0.75                      |
| $C_{2o}$                          | 1              | 1                         | 1                         |
| $V_e$ (eV)                        | -28.79214      | -107.32728                | -70.41425                 |
| $V_p$ (eV)                        | 9.33352        | 38.92728                  | 25.78002                  |
| $T$ (eV)                          | 6.77464        | 32.53914                  | 21.06675                  |
| $V_m$ (eV)                        | -3.38732       | -16.26957                 | -10.53337                 |
| $E_{(AO/HO)}$ (eV)                | -15.56407      | -15.56407                 | -15.56407                 |
| $\Delta E_{H_2MO(AO/HO)}$ (eV)    | 0              | 0                         | 0                         |
| $E_T(AO/HO)$ (eV)                 | -15.56407      | -15.56407                 | -15.56407                 |
| $E_T(H_2MO)$ (eV)                 | -31.63537      | -67.69451                 | -49.66493                 |
| $E_T(atom - atom, msp^3.AO)$ (eV) | -1.85836       | 0                         | 0                         |
| $E_T(MO)$ (eV)                    | -33.49373      | -67.69450                 | -49.66493                 |
| $\omega$ ( $10^{15}$ rad / s)     | 9.43699        | 24.9286                   | 24.2751                   |
| $E_K$ (eV)                        | 6.21159        | 16.40846                  | 15.97831                  |
| $\bar{E}_D$ (eV)                  | -0.16515       | -0.25352                  | -0.25017                  |
| $\bar{E}_{Kvib}$ (eV)             | 0.12312 [2]    | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) |
| $\bar{E}_{osc}$ (eV)              | -0.10359       | -0.22757                  | -0.14502                  |
| $E_{mag}$ (eV)                    | 0.14803        | 0.14803                   | 0.14803                   |
| $E_T(Group)$ (eV)                 | -33.59732      | -67.92207                 | -49.80996                 |
| $E_{initial}(c_1 AO/HO)$ (eV)     | -14.63489      | -14.63489                 | -14.63489                 |
| $E_{initial}(c_5 AO/HO)$ (eV)     | 0              | -13.59844                 | -13.59844                 |
| $E_D(Group)$ (eV)                 | 4.32754        | 12.49186                  | 7.83016                   |



BRANCHED ALKANES ( $C_nH_{2n+2}$ ,  $n = 3, 4, 5 \dots \infty$ )

The branched-chain alkanes,  $C_nH_{2n+2}$ , comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-alkane groups are solved using the same principles as those used to solve the methyl and methylene functional groups wherein the  $2s$  and  $2p$  AOs of each  $C$  hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy.  $E_r(atom-atom, msp^3.AO)$  of each  $C-C$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  atoms to the MO is  $-1.85836 eV$  or  $-1.44915 eV$  based on the energy match between the  $C2sp^3$  HOs corresponding to the energy contributions equivalent to those of methylene,  $-0.92918 eV$  (Eq. (14.513), or methyl,  $-0.72457 eV$  (Eq. (14.151)), groups, respectively.

The symbols of the functional groups of branched-chain alkanes are given in Table 15.9. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkanes are given in Tables 15.10, 15.11, and 15.12, respectively. The total energy of each branched-chain alkane given in Table 15.13 was calculated as the sum over the integer multiple of each  $E_D(group)$  of Table 15.12 corresponding to functional-group composition of the molecule. The bond angle parameters of branched-chain alkanes determined using Eqs. (15.79-15.108) are given in Table 15.14.

Table 15.9. The symbols of functional groups of branched alkanes.

| Functional Group      | Group Symbol   |
|-----------------------|----------------|
| CH <sub>3</sub> group | $C - H (CH_3)$ |
| CH <sub>2</sub> group | $C - H (CH_2)$ |
| CH                    | $C - H$        |
| CC bond (n-C)         | $C - C$ (a)    |
| CC bond (iso-C)       | $C - C$ (b)    |
| CC bond (tert-C)      | $C - C$ (c)    |
| CC (iso to iso-C)     | $C - C$ (d)    |
| CC (t to t-C)         | $C - C$ (e)    |
| CC (t to iso-C)       | $C - C$ (f)    |

Table 15.10. The geometrical bond parameters of branched alkanes and experimental values [1].

| Parameter                      | C-H (C <sub>H</sub> )<br>Group | C-H (C <sub>H</sub> )<br>Group | C-C (a)<br>Group | C-C (b)<br>Group | C-C (c)<br>Group | C-C (d)<br>Group | C-C (e)<br>Group | C-C (f)<br>Group |
|--------------------------------|--------------------------------|--------------------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| $a$ (Å)                        | 1.0974                         | 1.0974                         | 1.54280          | 1.54280          | 1.53635          | 1.54280          | 1.53635          | 1.53635          |
| $c'$ (Å)                       | 1.0974                         | 1.0974                         | 1.54280          | 1.54280          | 1.53635          | 1.54280          | 1.53635          | 1.53635          |
| Bond Length<br>2c' (Å)         | 1.0974                         | 1.0974                         | 1.54280          | 1.54280          | 1.53635          | 1.54280          | 1.53635          | 1.53635          |
| Exp. Bond Length<br>Length (Å) | 1.0974                         | 1.0974                         | 1.54280          | 1.54280          | 1.53635          | 1.54280          | 1.53635          | 1.53635          |
| $h, c$ (Å)                     | 1.27295                        | 1.27295                        | 1.54616          | 1.54616          | 1.52750          | 1.54616          | 1.52750          | 1.52750          |
| $\sigma$                       | 0.63380                        | 0.63380                        | 0.68600          | 0.68600          | 0.68888          | 0.68600          | 0.68888          | 0.68888          |

Table 15.11. The MO to HO intercept geometrical bond parameters of branched-chain alkanes.  $R, R', R''$  are H or alkyl groups.  $E_r$  is  $E_r(atom - atom, msp, AO)$ .

| Bond                                                                                                     | Atom           | $E_r$<br>(eV)<br>Bond 1 | $E_r$<br>(eV)<br>Bond 2 | $E_r$<br>(eV)<br>Bond 3 | $E_r$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>(eV) | $r_{final}$<br>(Å) | $r_{final}$<br>(Å) | $E_{atom}(C2sp^3)$<br>(eV)<br>Final | $E(C2sp^3)$<br>(eV)<br>Final | $\theta'$<br>(°) | $\theta_1$<br>(°) | $\theta_2$<br>(°) | $d_1$<br>(Å) | $d_2$<br>(Å) |
|----------------------------------------------------------------------------------------------------------|----------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------------|--------------------|--------------------|-------------------------------------|------------------------------|------------------|-------------------|-------------------|--------------|--------------|
| C-H (C <sub>H</sub> )                                                                                    | C              | -0.92918                | 0                       | 0                       | 0                       | -152.54487                    | 0.91771            | 0.86359            | -15.74493                           | -15.56407                    | 77.49            | 102.51            | 41.48             | 1.23564      | 0.18708      |
| C-H (C <sub>H</sub> )                                                                                    | C              | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                    | 0.91771            | 0.81549            | -16.68412                           | -16.49325                    | 68.47            | 111.53            | 35.84             | 1.35486      | 0.29933      |
| C-H (CH)                                                                                                 | C              | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                    | 0.91771            | 0.77247            | -17.61330                           | -17.42244                    | 61.10            | 118.90            | 31.37             | 1.42988      | 0.37326      |
| H <sub>1</sub> C <sub>1</sub> C <sub>2</sub> H <sub>2</sub> C <sub>3</sub> H <sub>3</sub><br>(C-C (a))   | C <sub>1</sub> | -0.92918                | 0                       | 0                       | 0                       | -152.54487                    | 0.91771            | 0.86359            | -15.74493                           | -15.56407                    | 63.82            | 116.18            | 30.08             | 1.83879      | 0.38106      |
| H <sub>1</sub> C <sub>1</sub> C <sub>2</sub> H <sub>2</sub> C <sub>3</sub> H <sub>3</sub><br>(C-C (b))   | C <sub>2</sub> | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                    | 0.91771            | 0.81549            | -16.68412                           | -16.49325                    | 56.41            | 123.59            | 26.06             | 1.90890      | 0.45117      |
| R-H <sub>1</sub> C <sub>1</sub> C <sub>2</sub> H <sub>2</sub> C <sub>3</sub> H <sub>3</sub><br>(C-C (c)) | C <sub>1</sub> | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                    | 0.91771            | 0.77247            | -17.61330                           | -17.42244                    | 48.30            | 131.70            | 21.90             | 1.97162      | 0.51388      |
| R-H <sub>1</sub> C <sub>1</sub> C <sub>2</sub> H <sub>2</sub> C <sub>3</sub> H <sub>3</sub><br>(C-C (d)) | C <sub>2</sub> | -0.92918                | -0.92918                | -0.92918                | -0.72457                | -154.71860                    | 0.91771            | 0.73889            | -17.92866                           | -17.73779                    | 48.21            | 131.79            | 21.74             | 1.95734      | 0.50570      |
| R-H <sub>1</sub> C <sub>1</sub> C <sub>2</sub> H <sub>2</sub> C <sub>3</sub> H <sub>3</sub><br>(C-C (e)) | C <sub>3</sub> | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                    | 0.91771            | 0.77247            | -17.61330                           | -17.42244                    | 48.30            | 131.70            | 21.90             | 1.97162      | 0.51388      |
| R-H <sub>1</sub> C <sub>1</sub> C <sub>2</sub> H <sub>2</sub> C <sub>3</sub> H <sub>3</sub><br>(C-C (f)) | C <sub>4</sub> | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.51399                    | 0.91771            | 0.76765            | -17.92866                           | -17.73779                    | 50.04            | 129.96            | 22.66             | 1.94462      | 0.49298      |
| R-H <sub>1</sub> C <sub>1</sub> C <sub>2</sub> H <sub>2</sub> C <sub>3</sub> H <sub>3</sub><br>(C-C (g)) | C <sub>5</sub> | -0.72457                | -0.72457                | -0.92918                | 0                       | -154.19863                    | 0.91771            | 0.79155            | -17.40869                           | -17.21763                    | 52.78            | 127.22            | 24.04             | 1.92443      | 0.47279      |
| R-H <sub>1</sub> C <sub>1</sub> C <sub>2</sub> H <sub>2</sub> C <sub>3</sub> H <sub>3</sub><br>(C-C (h)) | C <sub>6</sub> | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.51399                    | 0.91771            | 0.76765            | -17.92866                           | -17.73779                    | 50.04            | 129.96            | 22.66             | 1.94462      | 0.49298      |

Table 15.12. The energy parameters (eV) of functional groups of branched-chain alkanes.

| Parameters                               | $CH_3$<br>Group           | $CH_2$<br>Group           | $C-H$<br>Group            | $C-C(a)$<br>Group | $C-C(b)$<br>Group | $C-C(c)$<br>Group | $C-C(d)$<br>Group | $C-C(e)$<br>Group | $C-C(f)$<br>Group |
|------------------------------------------|---------------------------|---------------------------|---------------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| $n_1$                                    | 3                         | 2                         | 1                         | 1                 | 1                 | 1                 | 1                 | 1                 | 1                 |
| $n_2$                                    | 2                         | 1                         | 0                         | 0                 | 0                 | 0                 | 0                 | 0                 | 0                 |
| $n_3$                                    | 0                         | 0                         | 0                         | 0                 | 0                 | 0                 | 0                 | 0                 | 0                 |
| $C_1$                                    | 0.75                      | 0.75                      | 0.75                      | 0.5               | 0.5               | 0.5               | 0.5               | 0.5               | 0.5               |
| $C_2$                                    | 1                         | 1                         | 1                         | 1                 | 1                 | 1                 | 1                 | 1                 | 1                 |
| $c_1$                                    | 1                         | 1                         | 1                         | 1                 | 1                 | 1                 | 1                 | 1                 | 1                 |
| $c_2$                                    | 0.91771                   | 0.91771                   | 0.91771                   | 0.91771           | 0.91771           | 0.91771           | 0.91771           | 0.91771           | 0.91771           |
| $c_3$                                    | 0                         | 1                         | 1                         | 0                 | 0                 | 0                 | 1                 | 1                 | 0                 |
| $c_4$                                    | 1                         | 1                         | 1                         | 2                 | 2                 | 2                 | 2                 | 2                 | 2                 |
| $c_5$                                    | 3                         | 2                         | 1                         | 0                 | 0                 | 0                 | 0                 | 0                 | 0                 |
| $C_{10}$                                 | 0.75                      | 0.75                      | 0.75                      | 0.5               | 0.5               | 0.5               | 0.5               | 0.5               | 0.5               |
| $C_{30}$                                 | 1                         | 1                         | 1                         | 1                 | 1                 | 1                 | 1                 | 1                 | 1                 |
| $V_r$ (eV)                               | -107.32728                | -70.41425                 | -35.12015                 | -28.79214         | -28.79214         | -29.10112         | -28.79214         | -29.10112         | -29.10112         |
| $V_p$ (eV)                               | 38.92728                  | 25.78002                  | 12.87680                  | 9.33352           | 9.33352           | 9.37273           | 9.33352           | 9.37273           | 9.37273           |
| $T$ (eV)                                 | 32.53914                  | 21.06675                  | 10.48582                  | 6.77464           | 6.77464           | 6.90500           | 6.77464           | 6.90500           | 6.90500           |
| $V_n$ (eV)                               | -16.26957                 | -10.53337                 | -5.24291                  | -3.38732          | -3.38732          | -3.45250          | -3.38732          | -3.45250          | -3.45250          |
| $E'_{\text{atom}}$ (eV)                  | -15.56407                 | -15.56407                 | -14.63489                 | -15.56407         | -15.56407         | -15.35946         | -15.56407         | -15.35946         | -15.35946         |
| $\Delta E_{H_{1,2,3}}(atom)$ (eV)        | 0                         | 0                         | 0                         | 0                 | 0                 | 0                 | 0                 | 0                 | 0                 |
| $E_T(1,atom)$ (eV)                       | -15.56407                 | -15.56407                 | -14.63489                 | -15.56407         | -15.56407         | -15.35946         | -15.56407         | -15.35946         | -15.35946         |
| $E_T(1,2,atom)$ (eV)                     | -67.69451                 | -49.66493                 | -31.63533                 | -31.63537         | -31.63537         | -31.63535         | -31.63537         | -31.63535         | -31.63535         |
| $E_T(1,atom, msp, AO)$ (eV)              | 0                         | 0                         | 0                         | -1.85836          | -1.85836          | -1.44915          | -1.85836          | -1.44915          | -1.44915          |
| $E_T(1,2,atom)$ (eV)                     | -67.69450                 | -49.66493                 | -31.63537                 | -33.49373         | -33.49373         | -33.08452         | -33.49373         | -33.08452         | -33.08452         |
| $\omega$ ( $10^{15}$ rad/s)              | 24.9286                   | 24.2751                   | 24.1759                   | 9.43699           | 9.43699           | 15.4846           | 9.43699           | 9.55643           | 9.55643           |
| $E_k$ (eV)                               | 16.40846                  | 15.97831                  | 15.91299                  | 6.21159           | 6.21159           | 10.19220          | 6.21159           | 6.29021           | 6.29021           |
| $\bar{E}_n$ (eV)                         | -0.25352                  | -0.25017                  | -0.24966                  | -0.16515          | -0.16515          | -0.20896          | -0.16515          | -0.16416          | -0.16416          |
| $\bar{E}_{\text{rot}}$ (eV)              | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.35532<br>(Eq. (13.458)) | 0.12312<br>[2]    | 0.17978<br>[4]    | 0.09944<br>[5]    | 0.12312<br>[2]    | 0.12312<br>[2]    | 0.12312<br>[2]    |
| $\bar{E}_{\text{osc}}$ (eV)              | -0.22757                  | -0.14502                  | -0.07200                  | -0.10359          | -0.07526          | -0.15924          | -0.10359          | -0.10260          | -0.10260          |
| $E_{\text{mag}}$ (eV)                    | 0.14803                   | 0.14803                   | 0.14803                   | 0.14803           | 0.14803           | 0.14803           | 0.14803           | 0.14803           | 0.14803           |
| $E_T(1,2,atom)$ (eV)                     | -67.92207                 | -49.80996                 | -31.70737                 | -33.59732         | -33.49373         | -33.24376         | -33.59732         | -33.18712         | -33.18712         |
| $E_{\text{rot}}$ ( $\omega, atom$ ) (eV) | -14.63489                 | -14.63489                 | -14.63489                 | -14.63489         | -14.63489         | -14.63489         | -14.63489         | -14.63489         | -14.63489         |
| $E_{\text{rot}}$ ( $\omega, atom$ ) (eV) | -13.59844                 | -13.59844                 | -13.59844                 | 0                 | 0                 | 0                 | 0                 | 0                 | 0                 |
| $E_D(1,2,atom)$ (eV)                     | 12.49186                  | 7.83016                   | 3.32601                   | 4.32754           | 4.29921           | 3.97398           | 4.17951           | 3.62128           | 3.91734           |

Table 15.13. The total bond energies of branched alkanes calculated using the functional group composition and the energies of Table 15.12 compared to the experimental values [3].

| Formula                         | Name                       | CH <sub>3</sub> | CH <sub>2</sub> | CH | C-C (a) | C-C (b) | C-C (c) | C-C (d) | C-C (e) | C-C (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---------------------------------|----------------------------|-----------------|-----------------|----|---------|---------|---------|---------|---------|---------|-----------------------------------|-------------------------------------|----------------|
| C <sub>4</sub> H <sub>10</sub>  | Isobutane                  | 3               | 0               | 1  | 0       | 3       | 0       | 0       | 0       | 0       | 53.69922                          | 53.695                              | -0.00007       |
| C <sub>5</sub> H <sub>12</sub>  | Isopentane                 | 3               | 1               | 1  | 1       | 3       | 0       | 0       | 0       | 0       | 65.85692                          | 65.843                              | -0.00021       |
| C <sub>5</sub> H <sub>12</sub>  | Neopentane                 | 4               | 0               | 0  | 0       | 0       | 4       | 0       | 0       | 0       | 65.86336                          | 65.992                              | 0.00195        |
| C <sub>6</sub> H <sub>14</sub>  | 2-Methylpentane            | 3               | 2               | 1  | 2       | 3       | 0       | 0       | 0       | 0       | 78.01462                          | 78.007                              | -0.00010       |
| C <sub>6</sub> H <sub>14</sub>  | 3-Methylpentane            | 3               | 2               | 1  | 2       | 3       | 0       | 0       | 0       | 0       | 78.01462                          | 77.979                              | -0.00046       |
| C <sub>6</sub> H <sub>14</sub>  | 2,2-Dimethylbutane         | 4               | 1               | 0  | 1       | 0       | 4       | 0       | 0       | 0       | 78.02106                          | 78.124                              | 0.00132        |
| C <sub>6</sub> H <sub>14</sub>  | 2,3-Dimethylbutane         | 4               | 1               | 0  | 0       | 0       | 4       | 1       | 0       | 0       | 77.99581                          | 78.043                              | 0.00061        |
| C <sub>7</sub> H <sub>16</sub>  | 2-Methylhexane             | 3               | 3               | 1  | 3       | 3       | 0       | 0       | 0       | 0       | 90.17232                          | 90.160                              | -0.00014       |
| C <sub>7</sub> H <sub>16</sub>  | 3-Methylhexane             | 3               | 3               | 1  | 3       | 3       | 0       | 0       | 0       | 0       | 90.17232                          | 90.127                              | -0.00051       |
| C <sub>7</sub> H <sub>16</sub>  | 3-Ethylpentane             | 3               | 3               | 1  | 3       | 3       | 0       | 0       | 0       | 0       | 90.17232                          | 90.108                              | -0.00072       |
| C <sub>7</sub> H <sub>16</sub>  | 2,2-Dimethylpentane        | 4               | 2               | 0  | 2       | 0       | 4       | 0       | 0       | 0       | 90.17876                          | 90.276                              | 0.00107        |
| C <sub>7</sub> H <sub>16</sub>  | 2,3-Dimethylpentane        | 4               | 2               | 0  | 2       | 0       | 3       | 0       | 0       | 1       | 90.22301                          | 90.262                              | 0.00044        |
| C <sub>7</sub> H <sub>16</sub>  | 2,4-Dimethylpentane        | 4               | 1               | 2  | 0       | 0       | 0       | 0       | 0       | 0       | 90.24488                          | 90.233                              | -0.00013       |
| C <sub>7</sub> H <sub>16</sub>  | 3,3-Dimethylpentane        | 4               | 2               | 0  | 2       | 0       | 4       | 0       | 0       | 0       | 90.17876                          | 90.227                              | 0.00054        |
| C <sub>7</sub> H <sub>16</sub>  | 2-Methylheptane            | 3               | 4               | 1  | 4       | 3       | 0       | 0       | 0       | 0       | 102.33002                         | 102.322                             | -0.00008       |
| C <sub>7</sub> H <sub>16</sub>  | 3-Methylheptane            | 3               | 4               | 1  | 4       | 3       | 0       | 0       | 0       | 0       | 102.33002                         | 102.293                             | -0.00036       |
| C <sub>7</sub> H <sub>16</sub>  | 4-Methylheptane            | 3               | 4               | 1  | 4       | 3       | 0       | 0       | 0       | 0       | 102.33002                         | 102.286                             | -0.00043       |
| C <sub>7</sub> H <sub>16</sub>  | 2,2-Dimethylhexane         | 4               | 3               | 0  | 3       | 0       | 4       | 0       | 0       | 0       | 102.30169                         | 102.274                             | -0.00027       |
| C <sub>7</sub> H <sub>16</sub>  | 2,3-Dimethylhexane         | 4               | 2               | 2  | 2       | 4       | 0       | 0       | 0       | 0       | 102.33646                         | 102.417                             | 0.00079        |
| C <sub>7</sub> H <sub>16</sub>  | 2,4-Dimethylhexane         | 4               | 2               | 2  | 1       | 6       | 0       | 0       | 0       | 0       | 102.31121                         | 102.306                             | -0.00005       |
| C <sub>7</sub> H <sub>16</sub>  | 2,5-Dimethylhexane         | 4               | 2               | 2  | 1       | 6       | 0       | 0       | 0       | 0       | 102.40258                         | 102.362                             | -0.00040       |
| C <sub>7</sub> H <sub>16</sub>  | 3,3-Dimethylhexane         | 4               | 3               | 0  | 3       | 0       | 4       | 0       | 0       | 0       | 102.40258                         | 102.396                             | -0.00006       |
| C <sub>7</sub> H <sub>16</sub>  | 3,4-Dimethylhexane         | 4               | 2               | 2  | 2       | 4       | 0       | 0       | 0       | 0       | 102.33646                         | 102.369                             | 0.00032        |
| C <sub>8</sub> H <sub>18</sub>  | 3-Ethyl-2-methylpentane    | 4               | 2               | 2  | 2       | 4       | 0       | 1       | 0       | 0       | 102.31121                         | 102.296                             | -0.00015       |
| C <sub>8</sub> H <sub>18</sub>  | 2,2,3-Trimethylpentane     | 4               | 3               | 0  | 3       | 0       | 4       | 0       | 0       | 0       | 102.31121                         | 102.277                             | -0.00033       |
| C <sub>8</sub> H <sub>18</sub>  | 2,2,3-Trimethylpentane     | 5               | 1               | 1  | 1       | 2       | 3       | 0       | 1       | 1       | 102.33646                         | 102.317                             | -0.00019       |
| C <sub>8</sub> H <sub>18</sub>  | 2,2,4-Trimethylpentane     | 5               | 1               | 1  | 1       | 2       | 3       | 0       | 0       | 0       | 102.38071                         | 102.370                             | -0.00010       |
| C <sub>8</sub> H <sub>18</sub>  | 2,3,3-Trimethylpentane     | 5               | 0               | 0  | 0       | 5       | 0       | 2       | 0       | 0       | 102.40902                         | 102.412                             | 0.00003        |
| C <sub>8</sub> H <sub>18</sub>  | 2,3,4-Trimethylpentane     | 6               | 0               | 0  | 0       | 0       | 6       | 0       | 0       | 0       | 102.38071                         | 102.332                             | -0.00048       |
| C <sub>8</sub> H <sub>18</sub>  | 2,2,3,3-Tetramethylbutane  | 5               | 1               | 3  | 0       | 0       | 0       | 1       | 0       | 0       | 102.29240                         | 102.342                             | 0.00049        |
| C <sub>8</sub> H <sub>18</sub>  | 2,3,5-Trimethylhexane      | 4               | 4               | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 102.41632                         | 102.433                             | 0.00016        |
| C <sub>8</sub> H <sub>18</sub>  | 3,3-Diethylpentane         | 4               | 4               | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 114.54147                         | 114.551                             | 0.00008        |
| C <sub>8</sub> H <sub>18</sub>  | 2,2,3,3-Tetramethylpentane | 6               | 0               | 0  | 0       | 0       | 6       | 0       | 0       | 0       | 114.49416                         | 114.455                             | -0.00034       |
| C <sub>8</sub> H <sub>18</sub>  | 2,2,3,4-Tetramethylpentane | 6               | 0               | 0  | 0       | 0       | 3       | 1       | 0       | 1       | 114.57402                         | 114.494                             | -0.00070       |
| C <sub>8</sub> H <sub>18</sub>  | 2,2,4,4-Tetramethylpentane | 6               | 1               | 0  | 0       | 0       | 8       | 0       | 0       | 1       | 114.51960                         | 114.492                             | -0.00024       |
| C <sub>8</sub> H <sub>18</sub>  | 2,3,3,4-Tetramethylpentane | 6               | 2               | 0  | 0       | 4       | 0       | 0       | 2       | 2       | 114.57316                         | 114.541                             | -0.00028       |
| C <sub>8</sub> H <sub>18</sub>  | 2-Methylheptane            | 3               | 6               | 1  | 6       | 3       | 0       | 0       | 0       | 0       | 114.58266                         | 114.484                             | -0.00086       |
| C <sub>9</sub> H <sub>20</sub>  | 5-Methylheptane            | 3               | 6               | 1  | 6       | 3       | 0       | 0       | 0       | 0       | 126.64542                         | 126.680                             | 0.00027        |
| C <sub>10</sub> H <sub>22</sub> |                            | 3               | 6               | 1  | 6       | 3       | 0       | 0       | 0       | 0       | 126.64542                         | 126.663                             | 0.00014        |

Table 15.14. The bond angle parameters of branched-chain alkanes and experimental values [1]. In the calculation of  $\theta_i$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(atom - atom, msp, AO)$ .

| Atoms of Angle                   | $2c'_1$<br>Bond 1<br>( $a_1$ ) | $2c'_2$<br>Bond 2<br>( $a_2$ ) | $2c'_3$<br>Terminal<br>Atoms<br>( $a_3$ ) | $E_{terminal}$<br>Atom 1 | Atom 1<br>Hybridization<br>Designation<br>(Table 15.3.A) | $c_2$<br>Atom 1 | $c_2$<br>Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c'_2$  | $E_T$<br>(eV) | $\theta_i$<br>( $^\circ$ ) | $\theta_j$<br>( $^\circ$ ) | Cal.<br>$\theta$<br>( $^\circ$ ) | Exp. $\theta$<br>( $^\circ$ )                                   |
|----------------------------------|--------------------------------|--------------------------------|-------------------------------------------|--------------------------|----------------------------------------------------------|-----------------|-----------------|-------|-------|-------|---------|---------------|----------------------------|----------------------------|----------------------------------|-----------------------------------------------------------------|
| Methylane<br>$\angle HC_aH$      | 2.11106                        | 2.11106                        | 3.4252                                    | -15.75493                | 7                                                        | H               | H               | 1     | 1     | 0.75  | 1.15796 | 0             |                            |                            | 108.44                           | 107<br>(propane)                                                |
| $\angle C_aC_bC_c$               |                                |                                |                                           |                          |                                                          |                 |                 |       |       |       |         |               | 69.51                      |                            | 110.49                           | 113.8<br>(propane)<br>110.8<br>(butane)<br>110.8<br>(isobutane) |
| $\angle C_aC_bH$                 |                                |                                |                                           |                          |                                                          |                 |                 |       |       |       |         |               |                            |                            | 110.49                           | 111.0<br>(butane)<br>111.4<br>(isobutane)                       |
| Methyl<br>$\angle HC_aH$         | 2.09711                        | 2.09711                        | 3.4252                                    | -15.75493                | 7                                                        | H               | H               | 1     | 1     | 0.75  | 1.15796 | 0             |                            |                            | 109.50                           |                                                                 |
| $\angle C_aC_bC_c$               |                                |                                |                                           |                          |                                                          |                 |                 |       |       |       |         |               | 70.56                      |                            | 109.44                           |                                                                 |
| $\angle C_aC_bH$                 |                                |                                |                                           |                          |                                                          |                 |                 |       |       |       |         |               | 70.56                      |                            | 109.44                           |                                                                 |
| $\angle C_aC_bC_c$<br>iso $C_a$  | 2.91547                        | 2.91547                        | 4.7958                                    | -16.68412                | 25                                                       | $C_c$           | $C_c$           | 1     | 1     | 1     | 0.81549 | -1.85836      |                            |                            | 110.67                           | 110.8<br>(isobutane)                                            |
| $\angle C_aC_bH$<br>iso $C_a$    | 2.91547                        | 2.11323                        | 4.1633                                    | -15.55033                | 5                                                        | $C_b$           | $C_b$           | 0.75  | 1     | 0.75  | 1.04887 | 0             |                            |                            | 110.76                           |                                                                 |
| $\angle C_aC_bH$<br>iso $C_a$    | 2.91547                        | 2.09711                        | 4.1633                                    | -15.55033                | 5                                                        | $C_b$           | $C_b$           | 0.75  | 1     | 0.75  | 1.04887 | 0             |                            |                            | 111.27                           | 111.4<br>(isobutane)                                            |
| $\angle C_aC_bC_c$<br>tert $C_a$ | 2.90327                        | 2.90327                        | 4.7958                                    | -15.55033                | 5                                                        | $C_b$           | $C_c$           | 0.75  | 1     | 0.75  | 1.04887 | -1.85836      |                            |                            | 111.27                           | 111.4<br>(isobutane)                                            |
| $\angle C_aC_bC_d$               |                                |                                |                                           |                          |                                                          |                 |                 |       |       |       |         |               | 72.50                      |                            | 107.50                           |                                                                 |



# ALKENES ( $C_nH_{2n}$ , $n = 3, 4, 5 \dots \infty$ )

The straight and branched-chain alkenes,  $C_nH_{2n}$ , comprise at least one carbon-carbon double bond comprising a functional group that is solved equivalently to the double bond of ethylene. The double bond may be bound to one, two, three, or four carbon single bonds that substitute for the hydrogen atoms of ethylene. Based on the condition of energy matching of the orbital, any magnetic energy due to unpaired electrons in the constituent fragments, and differences in oscillation in the transition state, three distinct functional groups can be identified:  $C$  vinyl single bond to  $-C(C)=C$ ,  $C$  vinyl single bond to  $-C(H)=C$ , and  $C$  vinyl single bond to  $-C(C)=CH_2$ . In addition,  $CH_2$  of the  $-C=CH_2$  moiety is an alkene functional group.

The alkyl portion of the alkene may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The  $n$ -alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and  $t$ -butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to  $t$ -butyl, and  $t$ -butyl to  $t$ -butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in alkenes are equivalent to those in branched-chain alkanes. The solution of the functional groups comprises the hybridization of the  $2s$  and  $2p$  AOs of each  $C$  to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy.  $E_r(atom-atom,msp^3.AO)$  of the  $C=C$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  atoms to the MO is equivalent to that of ethylene,  $-2.26759 eV$ , given by Eq. (14.247).  $E_r(atom-atom,msp^3.AO)$  of each  $C-C$ -bond MO in Eq. (15.52) is  $-1.85836 eV$  or  $-1.44915 eV$  based on the energy match between the  $C2sp^3$  HOs corresponding to the energy contributions equivalent to those of methylene,  $-0.92918 eV$  (Eq. (14.513), or methyl,  $-0.72457 eV$  (Eq. (14.151)), groups, respectively.

The symbols of the functional groups of alkenes are given in Table 15.15. The geometrical (Eqs. (15.1-15.5) and (15.41)), intercept (Eqs. (15.71-15.78)), and energy (Eqs.

(15.6-15.11) and (15.17-15.56)) parameters of alkenes are given in Tables 15.16, 15.17, and 15.18, respectively. The total energy of each alkene given in Table 15.19 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.18 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage 5, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_D(\text{Group})$  ( $eV$ ) values based on composition is given by Eq. (15.58). The bond angle parameters of alkenes determined using Eqs. (15.79-15.108) are given in Table 15.20.

Table 15.15. The symbols of functional groups of alkenes.

| Functional Group                             | Group Symbol                |
|----------------------------------------------|-----------------------------|
| CC double bond                               | C=C                         |
| C vinyl single bond to -C(C)=C               | C-C (i)                     |
| C vinyl single bond to -C(H)=C               | C-C (ii)                    |
| C vinyl single bond to -C(C)=CH <sub>2</sub> | C-C (iii)                   |
| CH <sub>2</sub> alkenyl group                | C-H (CH <sub>2</sub> ) (i)  |
| CH <sub>3</sub> group                        | C-H (CH <sub>3</sub> )      |
| CH <sub>3</sub> alkyl group                  | C-H (CH <sub>3</sub> ) (ii) |
| CH                                           | C-H                         |
| CC bond (n-C)                                | C-C (a)                     |
| CC bond (iso-C)                              | C-C (b)                     |
| CC bond (tert-C)                             | C-C (c)                     |
| CC (iso to iso-C)                            | C-C (d)                     |
| CC (t to t-C)                                | C-C (e)                     |
| CC (t to iso-C)                              | C-C (f)                     |

Table 15.16. The geometrical bond parameters of alkenes and experimental values [1].

| Parameter            | C=C Group                                       | C-C (i) Group       | C-C (ii) Group      | C-C (iii) Group     | C-H (CH <sub>2</sub> ) (i) Group                       | C-H (CH <sub>2</sub> ) (ii) Group                      | C-H (CH <sub>3</sub> ) Group                           | C-H (CH <sub>3</sub> ) (i) Group                       | C-H (CH <sub>3</sub> ) (ii) Group | C-H (CH <sub>3</sub> ) (iii) Group | C-H (CH <sub>3</sub> ) (iv) Group | C-H Group            | C-C (a) Group                           | C-C (b) Group                           | C-C (c) Group                           | C-C (d) Group                           | C-C (e) Group                           | C-C (f) Group                           |
|----------------------|-------------------------------------------------|---------------------|---------------------|---------------------|--------------------------------------------------------|--------------------------------------------------------|--------------------------------------------------------|--------------------------------------------------------|-----------------------------------|------------------------------------|-----------------------------------|----------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|
| $a$ (Å)              | 1.47228                                         | 2.04740             | 2.04740             | 2.04740             | 1.64010                                                | 1.64920                                                | 1.64920                                                | 1.67122                                                | 1.67165                           | 1.67165                            | 1.67165                           | 1.67165              | 2.12499                                 | 2.12499                                 | 2.10725                                 | 2.12499                                 | 2.10725                                 | 2.10725                                 |
| $c'$ (Å)             | 1.26661                                         | 1.43087             | 1.43087             | 1.43087             | 1.04566                                                | 1.04856                                                | 1.04856                                                | 1.05553                                                | 1.05661                           | 1.05661                            | 1.05661                           | 1.05661              | 1.45744                                 | 1.45744                                 | 1.45164                                 | 1.45744                                 | 1.45164                                 | 1.45164                                 |
| Bond Length          | 1.34052                                         | 1.51437             | 1.51437             | 1.51437             | 1.10668                                                | 1.10974                                                | 1.10974                                                | 1.11713                                                | 1.11827                           | 1.11827                            | 1.11827                           | 1.11827              | 1.54280                                 | 1.54280                                 | 1.53635                                 | 1.54280                                 | 1.53635                                 | 1.53635                                 |
| $2c'$ (Å)            | 1.342                                           | 1.508               | 1.508               | 1.508               | 1.10                                                   | 1.107                                                  | 1.107                                                  | 1.107                                                  | 1.122                             | 1.122                              | 1.122                             | 1.122                | 1.532                                   | 1.532                                   | 1.532                                   | 1.532                                   | 1.532                                   | 1.532                                   |
| Exp. Bond Length (Å) | 1.346<br>(2-butene)<br>1.349<br>(1,3-butadiene) | 1.508<br>(2-butene) | 1.508<br>(2-butene) | 1.508<br>(2-butene) | 1.108<br>(2-methylpropene)<br>1.108<br>(1,3-butadiene) | 1.107<br>(2-methylpropene)<br>1.117<br>(1,3-butadiene) | 1.107<br>(2-methylpropene)<br>1.117<br>(1,3-butadiene) | 1.107<br>(2-methylpropene)<br>1.117<br>(1,3-butadiene) | 1.122<br>(isobutane)              | 1.122<br>(isobutane)               | 1.122<br>(isobutane)              | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $h, c$ (Å)           | 0.75055                                         | 1.46439             | 1.46439             | 1.46439             | 1.26354                                                | 1.27795                                                | 1.27795                                                | 1.29569                                                | 1.29924                           | 1.29924                            | 1.29924                           | 1.29924              | 1.54616                                 | 1.54616                                 | 1.52750                                 | 1.54616                                 | 1.52750                                 | 1.52750                                 |
| $\sigma$             | 0.86030                                         | 0.69887             | 0.69887             | 0.69887             | 0.63756                                                | 0.63380                                                | 0.63380                                                | 0.63159                                                | 0.63095                           | 0.63095                            | 0.63095                           | 0.63095              | 0.68600                                 | 0.68600                                 | 0.68888                                 | 0.68600                                 | 0.68888                                 | 0.68888                                 |

Table 15.17. The MO to HO intercept geometrical bond parameters of alkenes.  $R_1$  is an alkyl group and  $R, R', R''$  are H or alkyl groups.  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{msp}, \text{AO})$ .

| Bond                                              | Atom  | $E_r$<br>(eV)<br>Bond 1 | $E_r$<br>(eV)<br>Bond 2 | $E_r$<br>(eV)<br>Bond 3 | $E_r$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>$C2sp^2$<br>(eV) | $r_{\text{final}}$<br>( $a_0$ ) | $E_{\text{C2sp}^2}$<br>(eV)<br>Final | $\theta^*$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | $d_1$<br>( $a_0$ ) | $d_2$<br>( $a_0$ ) |
|---------------------------------------------------|-------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------------------------|---------------------------------|--------------------------------------|----------------------------|----------------------------|----------------------------|--------------------|--------------------|
| $C_1(H)C_2 = C_3(H)C_4$                           | $C_2$ | -1.13380                | -0.92918                | 0                       | 0                       | -153.67867                                | 0.91771                         | -16.88873                            | 127.61                     | 52.39                      | 58.24                      | 0.77492            | 0.49168            |
| $C_2(H)C_3 = C_4(H)C_5$                           | $C_3$ | -1.13380                | 0                       | 0                       | 0                       | -152.70949                                | 0.91771                         | -15.95955                            | 120.84                     | 50.16                      | 60.70                      | 0.72040            | 0.54620            |
| $C_3(C_4)C_2 = C_4(H)C_5$                         | $C_4$ | -1.13380                | -0.72457                | -0.72457                | 0                       | -154.19863                                | 0.91771                         | -17.08869                            | 126.39                     | 53.61                      | 56.95                      | 0.80289            | 0.46371            |
| $R_1C_1(H)C_2 = C_3(C)C_4$                        | $C_3$ | -1.13380                | -0.72457                | -0.72457                | 0                       | -154.19863                                | 0.91771                         | -17.08869                            | 60.88                      | 119.12                     | 27.79                      | 1.81127            | 0.38039            |
| $R_1C_1(H)C_2 = C_3(C)C_4$<br>(C-C (i))           | $C_4$ | -0.72457                | -0.92918                | 0                       | 0                       | -153.26945                                | 0.91771                         | -16.47951                            | 67.40                      | 112.60                     | 31.36                      | 1.74821            | 0.31734            |
| $R_1C_1(H)C_2 = C_3(C)C_4$<br>(C-C (iii))         | $C_2$ | -1.13380                | -0.92918                | 0                       | 0                       | -153.67866                                | 0.91771                         | -16.88873                            | 64.57                      | 115.43                     | 29.79                      | 1.77684            | 0.34596            |
| $R_1C_1(H)C_2 = C_3(H)C_4$                        | $C_4$ | -0.92918                | -0.92918                | 0                       | 0                       | -153.47405                                | 0.91771                         | -16.68411                            | 65.99                      | 114.01                     | 30.58                      | 1.76270            | 0.33183            |
| $R_1C_1(H)C_2 = C_3(H)C_4$<br>(C-C (i))           | $C_1$ | -1.13380                | 0                       | 0                       | 0                       | -152.74949                                | 0.91771                         | -15.95955                            | 77.15                      | 102.85                     | 41.13                      | 1.23531            | 0.18965            |
| $C_1 - H (CH_2) (i)$                              | $C_1$ | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                | 0.91771                         | -15.75493                            | 77.49                      | 102.51                     | 41.48                      | 1.23564            | 0.18708            |
| $C_1 - H (CH_2) (ii)$                             | $C_1$ | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                | 0.91771                         | -16.68412                            | 68.47                      | 111.53                     | 35.84                      | 1.35486            | 0.29933            |
| $C_1 - H (CH_2) (iii)$                            | $C_1$ | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                | 0.91771                         | -17.61330                            | 61.10                      | 118.90                     | 31.37                      | 1.42988            | 0.37326            |
| $H_1C_1C_2H_2CH_2 -$<br>(C-C (e))                 | $C_2$ | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                | 0.91771                         | -15.75493                            | 63.82                      | 116.18                     | 30.08                      | 1.83879            | 0.38106            |
| $H_1C_1C_2H_2CH_2 -$<br>(C-C (e))                 | $C_2$ | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                | 0.91771                         | -16.68412                            | 56.41                      | 123.59                     | 26.06                      | 1.98890            | 0.45117            |
| $R - H_2C_1C_2(H_2C_2 - R')HC(H_2 -$<br>(C-C (b)) | $C_2$ | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                | 0.91771                         | -17.61330                            | 48.30                      | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| $R - H_2C_1C_2(H_2C_2 - R')HC(H_2 -$<br>(C-C (e)) | $C_2$ | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -154.17860                                | 0.91771                         | -17.92866                            | 48.21                      | 131.79                     | 21.74                      | 1.95734            | 0.50570            |
| $tert(C_1(H_2C_2 - R')HC(H_2 -$<br>(C-C (d))      | $C_1$ | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                | 0.91771                         | -17.61330                            | 48.30                      | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| $tert(C_1(H_2C_2 - R')HC(H_2 -$<br>(C-C (e))      | $C_1$ | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.51399                                | 0.91771                         | -17.92866                            | 50.04                      | 129.96                     | 22.66                      | 1.94462            | 0.49298            |
| $tert(C_1(H_2C_2 - R')HC(H_2 -$<br>(C-C (f))      | $C_1$ | -0.72457                | -0.92918                | -0.92918                | 0                       | -154.19863                                | 0.91771                         | -17.08869                            | 52.78                      | 127.22                     | 24.04                      | 1.92443            | 0.47279            |
| $tert(C_1(H_2C_2 - R')HC(H_2 -$<br>(C-C (f))      | $C_1$ | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.51399                                | 0.91771                         | -17.92866                            | 50.04                      | 129.96                     | 22.66                      | 1.94462            | 0.49298            |

Table 15.18. The energy parameters (eV) of functional groups of alkenes.

| Parameters                        | C=C<br>Group | C-C (i)<br>Group | C-C (ii)<br>Group | C-C (iii)<br>Group | CH <sub>2</sub> (i)<br>Group | CH <sub>3</sub><br>Group | CH <sub>2</sub> (ii)<br>Group | C-H<br>Group | C-C (a)<br>Group | C-C (b)<br>Group | C-C (c)<br>Group | C-C (d)<br>Group | C-C (e)<br>Group | C-C (f)<br>Group |
|-----------------------------------|--------------|------------------|-------------------|--------------------|------------------------------|--------------------------|-------------------------------|--------------|------------------|------------------|------------------|------------------|------------------|------------------|
| $n_1$                             | 2            | 1                | 1                 | 1                  | 2                            | 3                        | 2                             | 1            | 1                | 1                | 1                | 1                | 1                | 1                |
| $n_2$                             | 0            | 0                | 0                 | 0                  | 1                            | 2                        | 1                             | 0            | 0                | 0                | 0                | 0                | 0                | 0                |
| $n_3$                             | 0            | 0                | 0                 | 0                  | 0                            | 0                        | 0                             | 0            | 0                | 0                | 0                | 0                | 0                | 0                |
| $C_1$                             | 0.5          | 0.5              | 0.5               | 0.5                | 0.75                         | 0.75                     | 0.75                          | 0.75         | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              |
| $C_2$                             | 0.91771      | 1                | 1                 | 1                  | 1                            | 1                        | 1                             | 1            | 1                | 1                | 1                | 1                | 1                | 1                |
| $c_1$                             | 1            | 1                | 1                 | 1                  | 1                            | 1                        | 1                             | 1            | 0.91771          | 0.91771          | 0.91771          | 0.91771          | 0.91771          | 0.91771          |
| $c_2$                             | 0.91771      | 0.91771          | 0.91771           | 0.91771            | 0.91771                      | -0.91771                 | 0.91771                       | 0.91771      | 0.91771          | 0.91771          | 0.91771          | 0.91771          | 0.91771          | 0.91771          |
| $c_3$                             | 0            | 1                | 0                 | 1                  | 1                            | 0                        | 1                             | 1            | 0                | 0                | 0                | 1                | 1                | 0                |
| $c_4$                             | 4            | 2                | 2                 | 2                  | 1                            | 1                        | 1                             | 1            | 2                | 2                | 2                | 2                | 2                | 2                |
| $c_5$                             | 0            | 0                | 0                 | 0                  | 2                            | 3                        | 2                             | 1            | 0                | 0                | 0                | 0                | 0                | 0                |
| $C_{10}$                          | 0.5          | 0.5              | 0.5               | 0.5                | 0.75                         | 0.75                     | 0.75                          | 0.75         | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              |
| $C_{10}$                          | 0.91771      | 1                | 1                 | 1                  | 1                            | 1                        | 1                             | 1            | 1                | 1                | 1                | 1                | 1                | 1                |
| $V_e$ (eV)                        | -102.08992   | -30.19634        | -30.19634         | -30.19634          | -72.03287                    | -107.32728               | -70.41425                     | -35.12015    | -28.79214        | -28.79214        | -29.10112        | -28.79214        | -29.10112        | -29.10112        |
| $V_f$ (eV)                        | 21.48386     | 9.50874          | 9.50874           | 9.50874            | 26.02344                     | 38.92728                 | 25.78002                      | 12.87680     | 9.33552          | 9.33552          | 9.37273          | 9.33552          | 9.37273          | 9.37273          |
| $T$ (eV)                          | 34.67062     | 7.37432          | 7.37432           | 7.37432            | 21.95990                     | 32.53914                 | 21.06675                      | 10.48582     | 6.77464          | 6.77464          | 6.90500          | 6.77464          | 6.90500          | 6.90500          |
| $V_m$ (eV)                        | -17.33531    | -3.68716         | -3.68716          | -3.68716           | -10.97995                    | -16.26957                | -10.53337                     | -5.24291     | -3.38732         | -3.38732         | -3.45250         | -3.38732         | -3.45250         | -3.45250         |
| $E_{(10100)}$ (eV)                | 0            | -14.63489        | -14.63489         | -14.63489          | -14.63489                    | -15.56407                | -15.56407                     | -14.63489    | -15.56407        | -15.56407        | -15.35946        | -15.56407        | -15.35946        | -15.35946        |
| $\Delta E_{11,100}$ (eV)          | 0            | 0                | 0                 | 0                  | 0                            | 0                        | 0                             | 0            | 0                | 0                | 0                | 0                | 0                | 0                |
| $E_{(10100)}$ (eV)                | 0            | -14.63489        | -14.63489         | -14.63489          | -14.63489                    | -15.56407                | -15.56407                     | -14.63489    | -15.56407        | -15.56407        | -15.35946        | -15.56407        | -15.35946        | -15.35946        |
| $E_{(11,10)}$ (eV)                | -63.27075    | -31.63534        | -31.63534         | -31.63534          | -49.66437                    | -67.69451                | -49.66493                     | -31.63533    | -31.63537        | -31.63537        | -31.63535        | -31.63537        | -31.63535        | -31.63535        |
| $E_{(atom - atom, msp, AO)}$ (eV) | -2.26759     | -1.44915         | -1.85836          | -1.44915           | 0                            | 0                        | 0                             | 0            | -1.85836         | -1.85836         | -1.44915         | -1.85836         | -1.44915         | -1.44915         |
| $E_{(101)}$ (eV)                  | -65.53833    | -33.08452        | -33.49373         | -33.08452          | -49.66493                    | -67.69450                | -49.66493                     | -31.63537    | -33.49373        | -33.49373        | -33.08452        | -33.49373        | -33.08452        | -33.08452        |
| $\omega$ (10 <sup>15</sup> rad/s) | 43.0680      | 9.97851          | 16.4962           | 9.97851            | 25.2077                      | 24.9286                  | 24.2751                       | 24.1759      | 9.43699          | 9.43699          | 15.4846          | 9.43699          | 9.55643          | 9.55643          |
| $E_c$ (eV)                        | 28.34813     | 6.58803          | 10.85807          | 6.58803            | 16.59214                     | 16.40846                 | 15.97831                      | 15.91299     | 6.21159          | 6.21159          | 10.19220         | 6.21159          | 6.29021          | 6.29021          |
| $\bar{E}_n$ (eV)                  | -0.34517     | -0.16774         | -0.21834          | -0.16774           | -0.25493                     | -0.25352                 | -0.25017                      | -0.24966     | -0.16515         | -0.16515         | -0.20896         | -0.16515         | -0.16416         | -0.16416         |
| $\bar{E}_{K\alpha}$ (eV)          | 0.17897      | 0.15895          | 0.09931           | 0.09931            | 0.35532                      | 0.35532                  | 0.35532                       | 0.35532      | 0.12312          | 0.12312          | 0.09944          | 0.12312          | 0.12312          | 0.12312          |
|                                   | [6]          | [7]              | [8]               | [8]                | Eq. (13.458)                 | Eq. (13.458)             | Eq. (13.458)                  | Eq. (13.458) | [2]              | [4]              | [5]              | [2]              | [2]              | [2]              |
| $\bar{E}_{\text{vac}}$ (eV)       | -0.25568     | -0.08827         | -0.16869          | -0.11809           | -0.07727                     | -0.22757                 | -0.14502                      | -0.07200     | -0.10359         | -0.07526         | -0.15924         | -0.10359         | -0.10260         | -0.10260         |
| $E_{\text{ring}}$ (eV)            | 0.14803      | 0.14803          | 0.14803           | 0.14803            | 0.14803                      | 0.14803                  | 0.14803                       | 0.14803      | 0.14803          | 0.14803          | 0.14803          | 0.14803          | 0.14803          | 0.14803          |
| $E_{(10100)}$ (eV)                | -66.04969    | -33.17279        | -33.66242         | -33.20260          | -49.81948                    | -67.92207                | -49.80996                     | -31.70737    | -33.59732        | -33.49373        | -33.24376        | -33.59732        | -33.18712        | -33.18712        |
| $E_{\text{ring}}$ (eV)            | -14.63489    | -14.63489        | -14.63489         | -14.63489          | -14.63489                    | -14.63489                | -14.63489                     | -14.63489    | -14.63489        | -14.63489        | -14.63489        | -14.63489        | -14.63489        | -14.63489        |
| $E_{\text{ring}}$ (eV)            | 0            | 0                | 0                 | 0                  | -13.59844                    | -13.59844                | -13.59844                     | -13.59844    | 0                | 0                | 0                | 0                | 0                | 0                |
| $E_p$ (eV)                        | 7.51014      | 3.75498          | 4.39264           | 3.78480            | 7.83968                      | 12.49186                 | 7.83016                       | 3.32601      | 4.32754          | 4.29921          | 3.97398          | 4.17951          | 3.62128          | 3.91734          |

Table 15.19. The total bond energies of alkenes calculated using the functional group composition and the energies of Table 15.18 compared to the experimental values [2]. The magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_{\sigma}(\text{group})$  ( $\text{eV}$ ) values based on composition is given by (15.58).

| Formula     | Name                         | $C=C$ | $C-C$ (i) | $C-C$ (ii) | $C-C$ (iii) | $CH_2$ (i) | $CH_3$ | $CH_2$ (ii) | $CH$ | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | $E_{mag}$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|-------------|------------------------------|-------|-----------|------------|-------------|------------|--------|-------------|------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------------------------------|-------------------------------------|----------------|
| $C_3H_6$    | Propene                      | 0     | 0         | 0          | 0           | 1          | 1      | 0           | 1    | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 35.56033                          | 35.63207                            | 0.00201        |
| $C_4H_8$    | 1-Butene                     | 1     | 0         | 0          | 0           | 1          | 1      | 1           | 1    | 1         | 0         | 0         | 0         | 0         | 0         | 0         | 47.78477                          | 47.78477                            | 0.00140        |
| $C_4H_8$    | trans-2-Butene               | 1     | 0         | 2          | 0           | 0          | 2      | 0           | 2    | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 47.90395                          | 47.90395                            | -0.00057       |
| $C_4H_8$    | Isobutene                    | 1     | 0         | 0          | 2           | 1          | 1      | 0           | 1    | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 47.96096                          | 47.96096                            | 0.00121        |
| $C_5H_{10}$ | 1-Pentene                    | 1     | 0         | 1          | 0           | 1          | 1      | 2           | 1    | 1         | 0         | 0         | 0         | 0         | 0         | 0         | 59.87573                          | 59.87573                            | 0.00125        |
| $C_5H_{10}$ | trans-2-Pentene              | 1     | 0         | 0          | 0           | 2          | 1      | 1           | 2    | 1         | 0         | 0         | 0         | 0         | 0         | 0         | 60.08886                          | 60.08886                            | -0.00043       |
| $C_5H_{10}$ | 2-Methyl-1-butene            | 1     | 0         | 2          | 0           | 1          | 2      | 1           | 1    | 1         | 0         | 0         | 0         | 0         | 0         | 0         | 60.06084                          | 60.09707                            | 0.00060        |
| $C_5H_{10}$ | 2-Methyl-2-butene            | 1     | 1         | 0          | 0           | 0          | 3      | 0           | 1    | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 60.21435                          | 60.16444                            | -0.00083       |
| $C_5H_{10}$ | 3-Methyl-1-butene            | 1     | 0         | 1          | 0           | 1          | 1      | 3           | 0    | 2         | 0         | 0         | 0         | 0         | 0         | 0         | 59.97662                          | 60.10127                            | 0.00068        |
| $C_6H_{12}$ | 1-Hexene                     | 1     | 0         | 1          | 0           | 1          | 1      | 3           | 1    | 3         | 0         | 0         | 0         | 0         | 0         | 0         | 72.03343                          | 72.12954                            | 0.00133        |
| $C_6H_{12}$ | trans-2-Hexene               | 1     | 0         | 2          | 0           | 0          | 2      | 2           | 2    | 2         | 0         | 0         | 0         | 0         | 0         | 0         | 72.24656                          | 72.23733                            | -0.00013       |
| $C_6H_{12}$ | trans-3-Hexene               | 1     | 0         | 0          | 2           | 1          | 2      | 2           | 2    | 2         | 0         | 0         | 0         | 0         | 0         | 0         | 72.24656                          | 72.24251                            | -0.00006       |
| $C_6H_{12}$ | trans-4-Hexene               | 1     | 0         | 2          | 0           | 1          | 2      | 2           | 2    | 2         | 0         | 0         | 0         | 0         | 0         | 0         | 72.21854                          | 72.29453                            | 0.00105        |
| $C_6H_{12}$ | 2-Methyl-1-pentene           | 1     | 0         | 0          | 2           | 1          | 1      | 1           | 1    | 1         | 2         | 0         | 0         | 0         | 0         | 0         | 72.37203                          | 72.37206                            | 0.00000        |
| $C_6H_{12}$ | 2-Methyl-2-pentene           | 1     | 2         | 1          | 0           | 0          | 3      | 1           | 1    | 1         | 2         | 0         | 0         | 0         | 0         | 0         | 72.13432                          | 72.19173                            | 0.00080        |
| $C_6H_{12}$ | 3-Methyl-1-pentene           | 1     | 0         | 1          | 0           | 1          | 2      | 1           | 2    | 1         | 3         | 0         | 0         | 0         | 0         | 0         | 72.10599                          | 72.21038                            | 0.00145        |
| $C_6H_{12}$ | 4-Methyl-1-pentene           | 1     | 0         | 1          | 0           | 1          | 2      | 1           | 2    | 0         | 3         | 0         | 0         | 0         | 0         | 0         | 72.37203                          | 72.33268                            | -0.00054       |
| $C_6H_{12}$ | 3-Methyl-trans-2-pentene     | 1     | 2         | 1          | 0           | 0          | 3      | 1           | 1    | 1         | 0         | 0         | 0         | 0         | 0         | 0         | 72.37203                          | 72.33268                            | -0.00054       |
| $C_6H_{12}$ | 4-Methyl-trans-2-pentene     | 1     | 0         | 2          | 0           | 0          | 3      | 0           | 3    | 0         | 2         | 0         | 0         | 0         | 0         | 0         | 72.34745                          | 72.31610                            | -0.00043       |
| $C_6H_{12}$ | pentene                      | 1     | 0         | 2          | 0           | 0          | 3      | 0           | 3    | 0         | 2         | 0         | 0         | 0         | 0         | 0         | 72.21854                          | 72.25909                            | 0.00056        |
| $C_6H_{12}$ | 2-Ethyl-1-butene             | 1     | 0         | 0          | 2           | 1          | 2      | 2           | 0    | 4         | 0         | 0         | 0         | 0         | 0         | 0         | 72.31943                          | 72.32543                            | 0.00008        |
| $C_6H_{12}$ | 2,3-Dimethyl-1-butene        | 1     | 0         | 0          | 2           | 1          | 3      | 0           | 1    | 0         | 2         | 0         | 0         | 0         | 0         | 0         | 72.31796                          | 72.30366                            | -0.00020       |
| $C_6H_{12}$ | 3,3-Dimethyl-1-butene        | 1     | 0         | 1          | 0           | 1          | 0      | 0           | 1    | 0         | 0         | 3         | 0         | 0         | -1        | 0         | 72.49750                          | 72.38450                            | -0.00156       |
| $C_6H_{12}$ | 2,3-Dimethyl-2-butene        | 1     | 4         | 0          | 0           | 0          | 4      | 0           | 0    | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 84.19113                          | 84.27084                            | 0.00095        |
| $C_7H_{14}$ | 1-Heptene                    | 1     | 0         | 1          | 0           | 1          | 1      | 4           | 1    | 4         | 0         | 0         | 0         | 0         | 0         | 0         | 84.26369                          | 84.30608                            | 0.00050        |
| $C_7H_{14}$ | 5-Methyl-1-hexene            | 1     | 0         | 1          | 0           | 1          | 1      | 2           | 2    | 1         | 3         | 0         | 0         | 0         | 0         | 0         | 84.52973                          | 84.42112                            | -0.00129       |
| $C_7H_{14}$ | trans-3-Methyl-3-hexene      | 1     | 2         | 1          | 0           | 0          | 3      | 2           | 1    | 2         | 0         | 0         | 0         | 0         | 0         | 0         | 84.44880                          | 84.49567                            | 0.00053        |
| $C_7H_{14}$ | 2,4-Dimethyl-1-pentene       | 1     | 0         | 0          | 2           | 1          | 3      | 1           | 1    | 0         | 3         | 0         | 0         | 0         | 0         | 0         | 84.27012                          | 84.47087                            | 0.00238        |
| $C_7H_{14}$ | 4,4-Dimethyl-1-pentene       | 1     | 0         | 1          | 0           | 1          | 3      | 1           | 1    | 0         | 0         | 4         | 0         | 0         | 0         | 0         | 84.63062                          | 84.54445                            | -0.00102       |
| $C_7H_{14}$ | 2,4-Dimethyl-2-pentene       | 1     | 2         | 1          | 0           | 0          | 4      | 0           | 2    | 0         | 2         | 0         | 0         | 0         | 0         | 0         | 84.63062                          | 84.54445                            | -0.00102       |
| $C_7H_{14}$ | trans-4,4-Dimethyl-2-pentene | 1     | 0         | 2          | 0           | 0          | 4      | 0           | 2    | 0         | 0         | 3         | 0         | 0         | -2        | 0         | 84.54076                          | 84.54549                            | 0.00006        |
| $C_7H_{14}$ | pentene                      | 1     | 0         | 2          | 0           | 0          | 4      | 0           | 2    | 0         | 2         | 0         | 0         | 0         | 0         | 0         | 84.47713                          | 84.44910                            | -0.00033       |
| $C_7H_{14}$ | 2-Ethyl-3-methyl-1-butene    | 1     | 0         | 0          | 2           | 1          | 3      | 1           | 1    | 1         | 2         | 0         | 0         | 0         | 0         | 0         | 84.51274                          | 84.51129                            | -0.00002       |
| $C_7H_{14}$ | 2,3,3-Trimethyl-1-butene     | 1     | 0         | 0          | 2           | 1          | 4      | 0           | 0    | 0         | 0         | 3         | 0         | 0         | -2        | 0         | 96.34883                          | 96.41421                            | 0.00068        |
| $C_7H_{14}$ | butene                       | 1     | 0         | 0          | 2           | 1          | 1      | 5           | 1    | 5         | 0         | 0         | 0         | 0         | 0         | 0         | 96.69846                          | 96.68782                            | -0.00011       |
| $C_7H_{14}$ | 1-Octene                     | 1     | 0         | 0          | 1           | 1          | 1      | 1           | 2    | 1         | 0         | 3         | 0         | 0         | 0         | 0         | 96.63483                          | 96.61113                            | -0.00025       |
| $C_7H_{14}$ | trans-2,2-Dimethyl-3-hexene  | 1     | 0         | 2          | 0           | 0          | 4      | 1           | 2    | 1         | 2         | 0         | 0         | 0         | 0         | 0         | 96.61293                          | 96.71684                            | 0.00107        |
| $C_8H_{16}$ | 3-Ethyl-2-methyl-1-pentene   | 1     | 0         | 0          | 2           | 1          | 3      | 2           | 1    | 2         | 2         | 0         | 0         | 0         | 0         | 0         | 96.67590                          | 96.65880                            | -0.00018       |
| $C_8H_{16}$ | 2,4,4-Trimethyl-1-pentene    | 1     | 0         | 0          | 2           | 1          | 4      | 1           | 0    | 0         | 0         | 4         | 0         | 0         | 0         | 0         | 120.74240                         | 120.74240                           | 0.00065        |
| $C_8H_{16}$ | 2,4,4-Trimethyl-2-pentene    | 0     | 2         | 1          | 0           | 0          | 5      | 0           | 1    | 0         | 0         | 3         | 0         | 0         | -3        | 0         | 120.66423                         | 145.07163                           | 0.00063        |
| $C_8H_{16}$ | pentene                      | 1     | 0         | 1          | 0           | 1          | 1      | 7           | 1    | 7         | 0         | 0         | 0         | 0         | 0         | 0         | 144.97963                         | 145.07163                           | 0.00063        |
| $C_8H_{16}$ | 1-Decene                     | 1     | 0         | 1          | 0           | 1          | 1      | 9           | 1    | 9         | 0         | 9         | 0         | 0         | 0         | 0         | 193.61043                         | 193.71766                           | 0.00055        |
| $C_8H_{16}$ | 1-Dodecene                   | 1     | 0         | 1          | 0           | 1          | 1      | 13          | 1    | 13        | 0         | 0         | 0         | 0         | 0         | 0         | 193.61043                         | 193.71766                           | 0.00055        |
| $C_8H_{16}$ | 1-Hexadecene                 | 1     | 0         | 1          | 0           | 1          | 1      | 13          | 1    | 13        | 0         | 0         | 0         | 0         | 0         | 0         | 193.61043                         | 193.71766                           | 0.00055        |

Table 15.20. The bond angle parameters of alkenes and experimental values [1]. In the calculation of  $\theta_e$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{msp}^3 \cdot \text{AO})$ .

| Atoms of Angle                                  | $2c'$<br>Bond 1<br>( $a_0$ ) | $2c'$<br>Bond 2<br>( $a_0$ ) | $2c'$<br>Terminal<br>Atoms<br>( $a_0$ ) | $E_{\text{Terminal Atom 1}}$<br>(eV) | Atom 1<br>Hybridization<br>Designation<br>(Table 15.3.A) | $E_{\text{Terminal Atom 2}}$ | Atom 2<br>Hybridization<br>Designation<br>(Table 15.3.A) | $c_1$<br>Atom 1 | $c_2$<br>Atom 2 | $C_1$ | $C_2$ | $\zeta_1$ | $\zeta_2$ | $E_p$<br>(eV) | $\theta_p$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | Cal. $\theta$<br>( $^\circ$ ) | Exp. $\theta$<br>( $^\circ$ )                                                                                                                                                                                                                                           |
|-------------------------------------------------|------------------------------|------------------------------|-----------------------------------------|--------------------------------------|----------------------------------------------------------|------------------------------|----------------------------------------------------------|-----------------|-----------------|-------|-------|-----------|-----------|---------------|----------------------------|----------------------------|----------------------------|-------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $\angle HC_n C_n$<br>( $C_n(H)C_n = C_n$ )      | 2.1123                       | 2.86175                      | 4.2895                                  | -15.95954<br>$C_n$                   | 9                                                        | -14.82575<br>$C_n$           | I                                                        | 0.85252         | 0.91771         | 0.75  | I     | 0.75      | 1.07647   | 0             |                            |                            |                            | 118.36                        |                                                                                                                                                                                                                                                                         |
| $\angle C_n C_n C_n$<br>( $C_n(C_n)C_n = C_n$ ) | 2.86175                      | 2.86175                      | 4.7958                                  | -16.68411<br>$C_n$                   | 24                                                       | -16.68411<br>$C_n$           | 24                                                       | 0.81549         | 0.81549         | I     | I     | I         | 0.81549   | -1.85836      |                            |                            |                            | 113.84                        |                                                                                                                                                                                                                                                                         |
| $\angle C_n C_n C_n$<br>( $C_n = C_n C_n$ )     | 2.5321                       | 2.86175                      | 4.7539                                  | -16.68873<br>$C_n$                   | 27                                                       | -16.68411<br>$C_n$           | 24                                                       | 0.80561         | 0.81549         | I     | I     | I         | 0.81055   | -1.85836      |                            |                            |                            | 123.46                        | 124.4<br>(1,3,5-hexatriene<br>CH <sub>2</sub> CH=CH-<br>CH=CH-CH <sub>2</sub> )<br>121.7<br>(1,3,5-hexatriene<br>CH <sub>2</sub> CH=CH-<br>CH=CH-CH <sub>2</sub> )<br>124.4<br>CaCPCc<br>(1,3-butadiene CCC)<br>125.3<br>(2-butene CH <sub>3</sub> CH=CH <sub>2</sub> ) |
| $\angle HC_n C_n$                               |                              |                              |                                         |                                      |                                                          |                              |                                                          |                 |                 |       |       |           |           |               |                            | 118.36                     | 123.46                     | 118.19                        |                                                                                                                                                                                                                                                                         |
| $\angle HC_n H$<br>( $H_2 C_n = C_n C_n$ )      | 2.04578                      | 2.04578                      | 3.4756                                  | -15.95955                            | 9                                                        | H                            | H                                                        | 0.85252         | I               | I     | I     | 0.75      | 1.17300   | 0             |                            |                            |                            | 116.31                        | 118.5<br>(2-methylpropene)                                                                                                                                                                                                                                              |
| $\angle C_n C_n H$<br>( $H_2 C_n = C_n C_n$ )   | 2.11106                      | 2.11106                      | 3.4252                                  | -15.75493                            | 7                                                        | H                            | H                                                        | 0.86359         | I               | I     | I     | 0.75      | 1.15796   | 0             |                            | 116.31                     |                            | 121.85                        | 121<br>(2-methylpropene)                                                                                                                                                                                                                                                |
| $\angle C_n C_n C_n$                            |                              |                              |                                         |                                      |                                                          |                              |                                                          |                 |                 |       |       |           |           |               |                            |                            |                            | 108.44                        | 107<br>(propane)                                                                                                                                                                                                                                                        |
| $\angle C_n C_n H$                              |                              |                              |                                         |                                      |                                                          |                              |                                                          |                 |                 |       |       |           |           |               | 69.51                      |                            |                            | 110.49                        | 113.8<br>(propane)<br>113.8<br>(butane)<br>110.8<br>(isobutane)<br>111.0<br>(butane)<br>111.4<br>(isobutane)                                                                                                                                                            |
| $\angle C_n C_n H$                              | 2.09711                      | 2.09711                      | 3.4252                                  | -15.75493                            | 7                                                        | H                            | H                                                        | 0.86359         | I               | I     | I     | 0.75      | 1.15796   | 0             |                            |                            |                            | 109.50                        |                                                                                                                                                                                                                                                                         |
| $\angle C_n C_n C_n$                            |                              |                              |                                         |                                      |                                                          |                              |                                                          |                 |                 |       |       |           |           |               |                            |                            |                            | 109.44                        |                                                                                                                                                                                                                                                                         |
| $\angle C_n C_n H$                              |                              |                              |                                         |                                      |                                                          |                              |                                                          |                 |                 |       |       |           |           |               |                            |                            |                            | 109.44                        |                                                                                                                                                                                                                                                                         |
| $\angle C_n C_n C_n$                            | 2.91547                      | 2.91547                      | 4.7958                                  | -16.68412<br>$C_n$                   | 25                                                       | -16.68412<br>$C_n$           | 25                                                       | 0.81549         | 0.81549         | I     | I     | I         | 0.81549   | -1.85836      |                            |                            |                            | 110.67                        | 110.8<br>(isobutane)                                                                                                                                                                                                                                                    |
| $\angle C_n C_n H$                              | 2.91547                      | 2.11323                      | 4.1633                                  | -15.55033<br>$C_n$                   | 5                                                        | -14.82575<br>$C_n$           | I                                                        | 0.87495         | 0.91771         | 0.75  | I     | 0.75      | 1.04887   | 0             |                            |                            |                            | 110.76                        |                                                                                                                                                                                                                                                                         |
| $\angle C_n C_n H$                              | 2.91547                      | 2.09711                      | 4.1633                                  | -15.55033<br>$C_n$                   | 5                                                        | -14.82575<br>$C_n$           | I                                                        | 0.87495         | 0.91771         | 0.75  | I     | 0.75      | 1.04887   | 0             |                            |                            |                            | 111.27                        | 111.4<br>(isobutane)                                                                                                                                                                                                                                                    |
| $\angle C_n C_n C_n$                            | 2.90227                      | 2.90327                      | 4.7958                                  | -15.55033<br>$C_n$                   | 5                                                        | -14.82575<br>$C_n$           | I                                                        | 0.87495         | 0.91771         | 0.75  | I     | 0.75      | 1.04887   | -1.85836      |                            |                            |                            | 111.27                        | 111.4<br>(isobutane)                                                                                                                                                                                                                                                    |
| $\angle C_n C_n C_n$                            |                              |                              |                                         |                                      |                                                          |                              |                                                          |                 |                 |       |       |           |           |               |                            | 72.50                      |                            | 107.50                        |                                                                                                                                                                                                                                                                         |

# ALKYNES ( $C_nH_{2n-2}$ , $n = 3, 4, 5, \dots, \infty$ )

The straight and branched-chain alkynes,  $C_nH_{2n-2}$ , have at least one carbon-carbon triple bond comprising a functional group that is solved equivalently to the triple bond of acetylene. The triple bond may be bound to one or two carbon single bonds that substitute for the hydrogen atoms of acetylene. Based on the energy matching of the mutually bound  $C$ , these  $C-C$ -bond MOs are defined as primary and secondary  $C-C$  functional groups, respectively, that are unique to alkynes. In addition, the corresponding terminal  $CH$  of a primary alkyne comprises a functional group that is solved equivalently to the methylene group of acetylene as given in the Acetylene Molecule section.

10 The alkyl portion of the alkyne may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The  $n$ -alkane  $C-C$  bond is the same as that of straight-chain alkanes. In 15 addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and  $t$ -butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to  $t$ -butyl, and  $t$ -butyl to  $t$ -butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in alkynes are equivalent to those in branched-chain alkanes.

The solution of the functional groups comprises the hybridization of the  $2s$  and  $2p$  20 AOs of each  $C$  to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy.  $E_r(atom-atom, msp^3.AO)$  of the  $C \equiv C$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  atoms to the MO is equivalent to that of acetylene,  $-3.13026 eV$ , given by Eq. (14.342).  $E_r(atom-atom, msp^3.AO)$  of each -alkyl-bond MO in 25 Eq. (15.52) is  $-1.85836 eV$  or  $-1.44915 eV$  based on the energy match between the  $C2sp^3$  HOs corresponding to the energy contributions equivalent to those of methylene,  $-0.92918 eV$  (Eq. (14.513)), or methyl,  $-0.72457 eV$  (Eq. (14.151)), groups, respectively. For the  $C-C$  groups each comprising a  $C$  single bond to  $C \equiv C$ ,  $E_r(atom-atom, msp^3.AO)$  is  $-0.72457 eV$  based on the energy match between the  $C2sp^3$  HOs for the mutually bound  $C$  of 30 the single and triple bonds. The parameter  $\omega$  of each group is matched for oscillation in the transition state based on the group being primary or secondary.



The symbols of the functional groups of alkynes are given in Table 15.21. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkynes are given in Tables 15.22, 15.23, and 15.24, respectively. The total energy of each alkyne given in Table 15.25 is calculated as the  
5 sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.24 corresponding to functional-group composition of the molecule. The bond angle parameters of alkynes determined using Eqs. (15.79-15.108) are given in Table 15.26. Each  $C$  of the  $C \equiv C$  group can further bond with only one atom, and the bond is linear as a minimum of energy as in the case of acetylene.

Table 15.21. The symbols of functional groups of alkynes.

| Functional Group                   | Group Symbol            |
|------------------------------------|-------------------------|
| CC triple bond                     | $C \equiv C$            |
| C single bond to $C \equiv C$ (1°) | C'-C' (i)               |
| C single bond to $C \equiv C$ (2°) | C'-C' (ii)              |
| CH (terminal)                      | C'-H (i)                |
| CH <sub>2</sub> group              | C'-H (CH <sub>2</sub> ) |
| CH <sub>3</sub> group              | C'-H (CH <sub>3</sub> ) |
| CH (alkyl)                         | C'-H (ii)               |
| CC bond (n-C)                      | C'-C' (a)               |
| CC bond (iso-C)                    | C'-C' (b)               |
| CC bond (tert-C)                   | C'-C' (c)               |
| CC (iso to iso-C)                  | C'-C' (d)               |
| CC (t to t-C)                      | C'-C' (e)               |
| CC (t to iso-C)                    | C'-C' (f)               |

Table 15.22. The geometrical bond parameters of alkynes and experimental values [1].

| Parameter                  | $C \equiv C$<br>Group                            | C'-C' (i)<br>Group       | C'-C' (ii)<br>Group      | C'-H (i)<br>Group    | C'-H (CH <sub>2</sub> )<br>Group                      | C'-H (CH <sub>3</sub> )<br>Group                      | C'-H (ii)<br>Group   | C'-C' (a)<br>Group                      | C'-C' (b)<br>Group                      | C'-C' (c)<br>Group                      | C'-C' (d)<br>Group                      | C'-C' (e)<br>Group                      | C'-C' (f)<br>Group                      |
|----------------------------|--------------------------------------------------|--------------------------|--------------------------|----------------------|-------------------------------------------------------|-------------------------------------------------------|----------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|
| $a$ (Å)                    | 1.28714                                          | 1.99185                  | 1.99185                  | 1.48719              | 1.67122                                               | 1.67465                                               | 2.12499              | 2.12499                                 | 2.12499                                 | 2.10725                                 | 2.12499                                 | 2.10725                                 | 2.10725                                 |
| $c'$ (Å)                   | 1.13452                                          | 1.41133                  | 1.41133                  | 0.99572              | 1.04856                                               | 1.05553                                               | 1.45744              | 1.45744                                 | 1.45744                                 | 1.45164                                 | 1.45744                                 | 1.45164                                 | 1.45164                                 |
| Bond Length<br>$2c'$ (Å)   | 1.20072                                          | 1.49369                  | 1.49369                  | 1.05383              | 1.10974                                               | 1.11713                                               | 1.11827              | 1.54280                                 | 1.54280                                 | 1.53635                                 | 1.54280                                 | 1.53635                                 | 1.53635                                 |
| Exp. Bond<br>Length<br>(Å) | 1.203<br>(acetylene)<br>1.208<br>(2,4-hexadiyne) | 1.450<br>(2,4-hexadiyne) | 1.450<br>(2,4-hexadiyne) | 1.060<br>(acetylene) | 1.107<br>(C-H<br>propane)<br>1.117<br>(C-H<br>butane) | 1.107<br>(C-H<br>propane)<br>1.117<br>(C-H<br>butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $h, c$ (Å)                 | 0.60793                                          | 1.40557                  | 1.40557                  | 1.10466              | 1.27295                                               | 1.29569                                               | 1.29924              | 1.54616                                 | 1.54616                                 | 1.52750                                 | 1.54616                                 | 1.52750                                 | 1.52750                                 |
| $e$                        | 0.88143                                          | 0.70855                  | 0.70855                  | 0.66953              | 0.63580                                               | 0.63159                                               | 0.63095              | 0.68600                                 | 0.68600                                 | 0.68888                                 | 0.68600                                 | 0.68888                                 | 0.68888                                 |

Table 15.23. The MO to HO intercept geometrical bond parameters of alkynes.  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{nspp}, \text{AO})$ .

| Bond                                      | Atom  | $E_r$<br>(eV)<br>Bond 1 | $E_r$<br>(eV)<br>Bond 2 | $E_r$<br>(eV)<br>Bond 3 | $E_r$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>$C2sp^3$<br>(eV) | $r_{\text{final}}$<br>( $a_0$ ) | $E_{\text{total}}(C2sp^3)$<br>(eV)<br>Final | $E(C2sp^3)$<br>(eV)<br>Final | $\theta^*$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | $d_t$<br>( $a_0$ ) | $d_z$<br>( $a_0$ ) |
|-------------------------------------------|-------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------------------------|---------------------------------|---------------------------------------------|------------------------------|----------------------------|----------------------------|----------------------------|--------------------|--------------------|
| $RC \equiv C \cdots H$                    | $C_u$ | -1.5613                 | 0                       | 0                       | 0                       | -153.18082                                | 0.83008                         | -16.39088                                   | -16.20002                    | 90.99                      | 89.01                      | 48.71                      | 0.98144            | 0.01428            |
| $C \cdots C \equiv C \cdots H$            | $C_u$ | -1.5613                 | -0.30229                | 0                       | 0                       | -153.54311                                | 0.81213                         | -16.75317                                   | -16.56231                    | 137.17                     | 42.83                      | 65.25                      | 0.53890            | 0.59562            |
| $C \cdots C \equiv C \cdots H$            | $C_u$ | -1.5613                 | 0                       | 0                       | 0                       | -153.18082                                | 0.83008                         | -16.39088                                   | -16.20002                    | 137.91                     | 42.09                      | 66.24                      | 0.51853            | 0.61599            |
| $C \cdots C \equiv C \cdots H$            | $C_u$ | -0.30229                | -0.92918                | 0                       | 0                       | -152.90716                                | 0.84418                         | -16.11722                                   | -15.92636                    | 75.71                      | 104.29                     | 35.59                      | 1.61974            | 0.20841            |
| $C \cdots H (CH_3)$                       | $C$   | -0.92918                | 0                       | 0                       | 0                       | -152.44487                                | 0.91771                         | -15.75493                                   | -15.56407                    | 77.49                      | 102.51                     | 41.48                      | 1.23564            | 0.18708            |
| $C \cdots H (CH_3)$                       | $C$   | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                | 0.91771                         | -16.68412                                   | -16.49325                    | 68.47                      | 111.53                     | 35.84                      | 1.35486            | 0.29933            |
| $C \cdots H (CH_3)$                       | $C$   | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                | 0.91771                         | -17.61330                                   | -17.42244                    | 61.10                      | 118.90                     | 31.37                      | 1.42988            | 0.37326            |
| $H_1C \cdots C_1H_2CH_3 -$<br>(C-C (a))   | $C_u$ | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                | 0.91771                         | -15.75493                                   | -15.56407                    | 63.82                      | 116.18                     | 30.08                      | 1.83879            | 0.38106            |
| $H_1C \cdots C_1H_2CH_3 -$<br>(C-C (a))   | $C_u$ | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                | 0.91771                         | -16.68412                                   | -16.49325                    | 56.41                      | 123.59                     | 26.06                      | 1.90890            | 0.45117            |
| $R-H_1C_1C_2(H_2C-R)HCH_3 -$<br>(C-C (b)) | $C_u$ | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                | 0.91771                         | -17.61330                                   | -17.42244                    | 48.30                      | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| $R-H_1C_1C_2(H_2C-R)HCH_3 -$<br>(C-C (b)) | $C_u$ | -0.92918                | -0.92918                | -0.92918                | -0.72457                | -154.71860                                | 0.91771                         | -17.92866                                   | -17.73779                    | 48.21                      | 131.79                     | 21.74                      | 1.97374            | 0.50570            |
| $HOHC_1C_2(H_2C-R)HCH_3 -$<br>(C-C (d))   | $C_u$ | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                | 0.91771                         | -17.61330                                   | -17.42244                    | 48.30                      | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| $HOHC_1C_2(H_2C-R)HCH_3 -$<br>(C-C (d))   | $C_u$ | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.51399                                | 0.91771                         | -17.92866                                   | -17.73779                    | 50.04                      | 129.96                     | 22.66                      | 1.94462            | 0.49298            |
| $HOHC_1C_2(H_2C-R)HCH_3 -$<br>(C-C (f))   | $C_u$ | -0.72457                | -0.92918                | -0.92918                | 0                       | -154.19663                                | 0.91771                         | -17.40869                                   | -17.21783                    | 52.78                      | 127.22                     | 24.04                      | 1.92443            | 0.47279            |
| $HOHC_1C_2(H_2C-R)HCH_3 -$<br>(C-C (f))   | $C_u$ | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.51399                                | 0.91771                         | -17.92866                                   | -17.73779                    | 50.04                      | 129.96                     | 22.66                      | 1.94462            | 0.49298            |

Table 15.24. The energy parameters (eV) of functional groups of alkyne.

| Parameters                        | C $\equiv$ C Group | C-C (i) Group | C-C (ii) Group | C-H (i) Group | CH <sub>3</sub> Group | CH <sub>2</sub> Group | C-H (ii) Group | C-C (a) Group | C-C (b) Group | C-C (c) Group | C-C (d) Group | C-C (e) Group | C-C (f) Group |
|-----------------------------------|--------------------|---------------|----------------|---------------|-----------------------|-----------------------|----------------|---------------|---------------|---------------|---------------|---------------|---------------|
| $n_1$                             | 3                  | 1             | 1              | 1             | 3                     | 2                     | 1              | 1             | 1             | 1             | 1             | 1             | 1             |
| $n_2$                             | 0                  | 0             | 0              | 0             | 2                     | 1                     | 0              | 0             | 0             | 0             | 0             | 0             | 0             |
| $n_3$                             | 0                  | 0             | 0              | 0             | 0                     | 0                     | 0              | 0             | 0             | 0             | 0             | 0             | 0             |
| $C_1$                             | 0.5                | 0.5           | 0.5            | 0.75          | 0.75                  | 0.75                  | 0.75           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           |
| $C_2$                             | 1                  | 1             | 1              | 1             | 1                     | 1                     | 1              | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_3$                             | 1                  | 1             | 1              | 1             | 1                     | 1                     | 1              | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_4$                             | 0.91771            | 0.91771       | 0.91771        | 0.91771       | 0.91771               | 0.91771               | 0.91771        | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       |
| $C_5$                             | 2                  | 1             | 1              | 0             | 0                     | 1                     | 1              | 0             | 0             | 0             | 1             | 1             | 0             |
| $C_6$                             | 6                  | 2             | 2              | 1             | 1                     | 1                     | 1              | 2             | 2             | 2             | 2             | 2             | 2             |
| $C_7$                             | 0                  | 0             | 0              | 1             | 3                     | 2                     | 1              | 0             | 0             | 0             | 0             | 0             | 0             |
| $C_{10}$                          | 0.5                | 0.5           | 0.5            | 0.75          | 0.75                  | 0.75                  | 0.75           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           |
| $C_{20}$                          | 1                  | 1             | 1              | 1             | 1                     | 1                     | 1              | 1             | 1             | 1             | 1             | 1             | 1             |
| $V_r$ (eV)                        | -182.53826         | -31.29307     | -31.29307      | -40.62396     | -107.32728            | -70.41425             | -35.12015      | -28.79214     | -28.79214     | -28.79214     | -28.79214     | -28.79214     | -29.10112     |
| $V_r$ (eV)                        | 35.97770           | 9.64042       | 9.64042        | 13.66428      | 38.92728              | 25.78002              | 12.87680       | 9.33352       | 9.33352       | 9.33352       | 9.33352       | 9.33352       | 9.37273       |
| $T$ (eV)                          | 70.90876           | 7.85528       | 7.85528        | 13.65796      | 32.53914              | 21.06675              | 10.48582       | 6.77464       | 6.77464       | 6.90500       | 6.77464       | 6.90500       | 6.90500       |
| $V_m$ (eV)                        | -35.45438          | -3.92764      | -3.92764       | -6.82898      | -16.26957             | -10.53337             | -5.24291       | -3.38732      | -3.38732      | -3.45250      | -3.38732      | -3.45250      | -3.45250      |
| $E_{(atom)}$ (eV)                 | -16.20002          | -14.63489     | -14.63489      | -14.63489     | -15.56407             | -15.56407             | -14.63489      | -15.56407     | -15.56407     | -15.35946     | -15.56407     | -15.35946     | -15.35946     |
| $\Delta E_{(atom)}$ (eV)          | 0                  | -0.72457      | -0.72457       | -3.13026      | 0                     | 0                     | 0              | 0             | 0             | 0             | 0             | 0             | 0             |
| $E_{(atom)}$ (eV)                 | -16.20002          | -13.91032     | -13.91032      | -11.50462     | -15.56407             | -15.56407             | -14.63489      | -15.56407     | -15.56407     | -15.35946     | -15.56407     | -15.35946     | -15.35946     |
| $E_{(atom)}$ (eV)                 | -94.90616          | -31.63533     | -31.63533      | -31.63533     | -67.69451             | -49.66493             | -31.63533      | -31.63537     | -31.63537     | -31.63535     | -31.63537     | -31.63535     | -31.63535     |
| $E_T$ (atom - atom, msp, AO) (eV) | -3.13026           | -0.72457      | -0.72457       | 0             | 0                     | 0                     | 0              | -1.85836      | -1.85836      | -1.44915      | -1.85836      | -1.44915      | -1.44915      |
| $E_T$ (eV)                        | -98.03637          | -32.35994     | -32.35994      | -31.63537     | -67.69450             | -49.66493             | -31.63537      | -33.49373     | -33.49373     | -33.08452     | -33.49373     | -33.08452     | -33.08452     |
| $\omega$ ( $10^5$ rad/s)          | 20.0186            | 10.3988       | 17.5426        | 30.8370       | 24.9286               | 24.2751               | 24.1759        | 9.43699       | 9.43699       | 15.4846       | 9.43699       | 9.55643       | 9.55643       |
| $E_K$ (eV)                        | 13.17659           | 6.84470       | 11.54682       | 20.29747      | 16.40846              | 15.97831              | 15.91299       | 6.21159       | 6.21159       | 10.19220      | 6.21159       | 6.29021       | 6.29021       |
| $E_D$ (eV)                        | -0.23468           | -0.16749      | -0.21754       | -0.28197      | -0.25352              | -0.25017              | -0.24966       | -0.16515      | -0.16515      | -0.20896      | -0.16515      | -0.16416      | -0.16416      |
| $E_{K_{max}}$ (eV)                | 0.27773            | 0.08989       | 0.08989        | 0.35532       | 0.35532               | 0.35532               | 0.35532        | 0.12312       | 0.17978       | 0.09944       | 0.12312       | 0.12312       | 0.12312       |
|                                   | [9]                | [9]           | [9]            | Eq. (13.458)  | Eq. (13.458)          | Eq. (13.458)          | Eq. (13.458)   | [2]           | [4]           | [5]           | [2]           | [2]           | [2]           |
| $E_{(atom)}$ (eV)                 | -0.09581           | -0.12255      | -0.17260       | -0.10430      | -0.22757              | -0.14502              | -0.07200       | -0.10359      | -0.07526      | -0.15924      | -0.10359      | -0.10260      | -0.10260      |
| $E_{(atom)}$ (eV)                 | 0.14803            | 0.14803       | 0.14803        | 0.14803       | 0.14803               | 0.14803               | 0.14803        | 0.14803       | 0.14803       | 0.14803       | 0.14803       | 0.14803       | 0.14803       |
| $E_{(atom)}$ (eV)                 | -98.02775          | -32.48249     | -32.53254      | -31.73967     | -67.92207             | -49.80996             | -31.70737      | -33.59732     | -33.49373     | -33.24376     | -33.59732     | -33.18712     | -33.18712     |
| $E_{(atom)}$ (eV)                 | -14.63489          | -14.63489     | -14.63489      | -14.63489     | -14.63489             | -14.63489             | -14.63489      | -14.63489     | -14.63489     | -14.63489     | -14.63489     | -14.63489     | -14.63489     |
| $E_{(atom)}$ (eV)                 | 0                  | 0             | 0              | -13.59844     | -13.59844             | -13.59844             | -13.59844      | 0             | 0             | 0             | 0             | 0             | 0             |
| $E_{(atom)}$ (eV)                 | 10.21841           | 3.21271       | 3.26276        | 3.50634       | 12.49186              | 7.83016               | 3.32601        | 4.32754       | 4.29921       | 3.97398       | 4.17951       | 3.62128       | 3.91734       |

Table 15.25. The total bond energies of alkynes calculated using the functional group composition and the energies of Table 15.24 compared to the experimental values [2].

| Formula  | Name     | $C \equiv C$ | $C \equiv C$<br>(i) | $C \equiv C$<br>(ii) | $C \equiv C$<br>(i) | $C \equiv C$<br>(ii) | $C \equiv C$<br>(i) | $C \equiv C$<br>(ii) | $C \equiv C$<br>(i) | $C \equiv C$<br>(ii) | $C \equiv C$<br>(i) | $C \equiv C$<br>(ii) | $C \equiv C$<br>(i) | $C \equiv C$<br>(ii) | Calculated<br>Total Bond Energy<br>(eV) | Experimental<br>Total Bond Energy<br>(eV) | Relative Error |
|----------|----------|--------------|---------------------|----------------------|---------------------|----------------------|---------------------|----------------------|---------------------|----------------------|---------------------|----------------------|---------------------|----------------------|-----------------------------------------|-------------------------------------------|----------------|
| $C_4H_4$ | Propyne  | 1            | 1                   | 0                    | 1                   | 1                    | 0                   | 0                    | 0                   | 0                    | 0                   | 0                    | 0                   | 0                    | 29.40332                                | 29.40332                                  | -0.00035       |
| $C_4H_6$ | 1-Butyne | 1            | 1                   | 0                    | 1                   | 1                    | 0                   | 0                    | 0                   | 0                    | 0                   | 0                    | 0                   | 0                    | 41.58702                                | 41.55495                                  | -0.00077       |
| $C_4H_6$ | 2-Butyne | 1            | 0                   | 2                    | 0                   | 2                    | 0                   | 0                    | 0                   | 0                    | 0                   | 0                    | 0                   | 0                    | 41.72765                                | 41.75705                                  | 0.00070        |
| $C_4H_6$ | 1-Nonyne | 1            | 1                   | 0                    | 1                   | 1                    | 0                   | 0                    | 0                   | 0                    | 0                   | 0                    | 0                   | 0                    | 102.37552                               | 102.35367                                 | -0.00021       |

Table 15.26. The bond angle parameters of alkynes and experimental values [1]. In the calculation of  $\theta_r$ , the parameters from the preceding angle were used.  $E_r$  is  $E_r(atom - atom, nsp^2, AO)$ .

| Atoms of Angle                                           | $2C'$<br>Bond 1<br>( $\alpha_0$ ) | $2C'$<br>Bond 2<br>( $\alpha_0$ ) | $2C'$<br>Terminal<br>Atoms<br>( $\alpha_0$ ) | $E_r$<br>Atom 1<br>(Table 15.3.A) | Atom 1<br>Hybridization<br>Designation<br>(Table 15.3.A) | $E_r$<br>Atom 2<br>(Table 15.3.A) | Atom 2<br>Hybridization<br>Designation<br>(Table 15.3.A) | $C_2$<br>Atom 1 | $C_2$<br>Atom 2 | $C_1$ | $C_2$ | $C_1$ | $C_2$   | $C_1$ | $C_2$ | $E_r$<br>(eV) | $\theta_r$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | Cal. $\theta$<br>( $^\circ$ ) | Exp. $\theta$<br>( $^\circ$ ) |
|----------------------------------------------------------|-----------------------------------|-----------------------------------|----------------------------------------------|-----------------------------------|----------------------------------------------------------|-----------------------------------|----------------------------------------------------------|-----------------|-----------------|-------|-------|-------|---------|-------|-------|---------------|----------------------------|----------------------------|----------------------------|-------------------------------|-------------------------------|
| $LC'_aC'_bC'_c$<br>( $C'_aC'_b \equiv C'_cH$ )<br>Methyl | 2.11106                           | 2.11106                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 180                           | 107<br>(propyne)              |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 108.44                        | 112<br>(propyne)              |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 110.49                        | 113.8<br>(butane)             |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.50                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 111.0<br>(butane)             |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 111.4<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.09711                           | 2.09711                           | 3.4252                                       | -15.75493                         | 7                                                        | H                                 | H                                                        | 0.86359         | 1               | 1     | 1     | 0.75  | 1.15796 | 0     |       |               |                            |                            |                            | 109.44                        | 110.8<br>(isobutane)          |
| $LC'_aC'_bC'_c$<br>Methyl                                | 2.0971                            |                                   |                                              |                                   |                                                          |                                   |                                                          |                 |                 |       |       |       |         |       |       |               |                            |                            |                            |                               |                               |

# ALKYL FLUORIDES ( $C_n H_{2n+2-m} F_m$ , $n=1,2,3,4,5\ldots\infty$ $m=1,2,3\ldots\infty$ )

The branched-chain alkyl fluorides,  $C_n H_{2n+2-m} F_m$ , may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds wherein at least one  $H$  is replaced by a fluorine. The  $C-F$  bond comprises a functional group for each case of  $F$  replacing a  $H$  of methane in the series  $H_{4-m} C - F_m$ ,  $m=1,2,3,4$ , and  $F$  replacing a  $H$  of an alkane. The methyl, methylene, methylene functional groups are equivalent to those of branched-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2 CH$ ) and t-butyl ( $(CH_3)_3 C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the  $C-F$  functional groups comprises the hybridization of the  $2s$  and  $2p$  AOs of each  $C$  to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the  $F$  AO to form a molecular orbital (MO) permits each participating orbital to decrease in radius and energy. In alkyl fluorides, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)), and the  $F$  AO has an energy of  $E(F) = -17.42282 \text{ eV}$ . To meet the equipotential condition of the union of the  $C-F$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the  $C-F$ -bond MO given by Eqs. (15.68) and (15.70) is

$$c_2(C2sp^3 HO \text{ to } F) = \frac{E(C, 2sp^3)}{E(F)} c_2(C2sp^3 HO) = \frac{-14.63489 \text{ eV}}{-17.42282 \text{ eV}} (0.91771) = 0.77087 \quad (15.110)$$

$E_r(\text{atom-atom}, msp^3.AO)$  of the  $C-F$ -bond MO in Eq. (15.52) based on the charge donation from  $F$  to the MO is determined by the linear combination that results in a energy that is a minimum which does not exceed the energy of the AO of the  $F$  atom to which it is energy matched.

The symbols of the functional groups of branched-chain alkyl fluorides are given in Table 15.27. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl fluorides are

given in Tables 15.28, 15.29, and 15.30, respectively. The total energy of each branched-chain alkyl fluoride given in Table 15.31 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.30 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_D(\text{Group})$  (eV) values based on composition is given by Eq. (15.58). In the case of trifluoromethane,  $E_{mag}$  is positive since the term due to the fluorine atoms cancels that of the  $CH$  group. The  $C-C$  bonds to the  $CHF$  group (one  $H$  bond to  $C$ ) were each treated as an iso  $C-C$  bond. The  $C-C$  bonds to the  $CF$  group (no  $H$  bonds to  $C$ ) were each treated as a tert-butyl  $C-C$ .  $E_{mag}$  was subtracted for each t-butyl group. The bond angle parameters of branched-chain alkyl fluorides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.110) are given in Table 15.32.

Table 15.27. The symbols of functional groups of branched-chain alkyl fluorides.

| Functional Group           | Group Symbol     |
|----------------------------|------------------|
| CF of $CF_m H_{4-m}$       | $C-F$ (i)        |
| CF of $C_n H_{2n+2-m} F_m$ | $C-F$ (ii)       |
| $CH_3$ group               | $C-H$ ( $CH_3$ ) |
| $CH_2$ group               | $C-H$ ( $CH_2$ ) |
| CH                         | $C-H$            |
| CC bond (n-C)              | $C-C$ (a)        |
| CC bond (iso-C)            | $C-C$ (b)        |
| CC bond (tert-C)           | $C-C$ (c)        |
| CC (iso to iso-C)          | $C-C$ (d)        |
| CC (t to t-C)              | $C-C$ (e)        |
| CC (t to iso-C)            | $C-C$ (f)        |

Table 15.28. The geometrical bond parameters of branched-chain alkyl fluorides and experimental values [1].

| Parameter                | C-F (i)<br>Group           | C-F (ii)<br>Group          | C-H (CH <sub>3</sub> )<br>Group | C-H (CH <sub>2</sub> )<br>Group | C-H (CH)<br>Group    | C-C (a)<br>Group   | C-C (b)<br>Group   | C-C (c)<br>Group   | C-C (d)<br>Group   | C-C (e)<br>Group   | C-C (f)<br>Group   |
|--------------------------|----------------------------|----------------------------|---------------------------------|---------------------------------|----------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| $a$ (Å)                  | 1.72139                    | 1.72139                    | 1.64920                         | 1.67122                         | 1.67465              | 2.12499            | 2.12499            | 2.10725            | 2.12499            | 2.10725            | 2.10725            |
| $c'$ (Å)                 | 1.31202                    | 1.31202                    | 1.04856                         | 1.05553                         | 1.05661              | 1.45744            | 1.45744            | 1.45164            | 1.45744            | 1.45164            | 1.45164            |
| Bond Length<br>$2c'$ (Å) | 1.38858                    | 1.38858                    | 1.10974                         | 1.11713                         | 1.11827              | 1.54280            | 1.54280            | 1.53635            | 1.54280            | 1.53635            | 1.53635            |
| Exp. Bond Length<br>(Å)  | 1.382<br>(methyl fluoride) | 1.382<br>(methyl fluoride) | 1.107<br>(C-H propane)          | 1.107<br>(C-H propane)          | 1.122<br>(isobutane) | 1.532<br>(propane) | 1.532<br>(propane) | 1.532<br>(propane) | 1.532<br>(propane) | 1.532<br>(propane) | 1.532<br>(propane) |
| $h_{C'}$ (Å)             | 1.11435                    | 1.11435                    | 1.27295                         | 1.29569                         | 1.29924              | 1.54616            | 1.54616            | 1.52750            | 1.54616            | 1.52750            | 1.52750            |
| $e$                      | 0.76219                    | 0.76219                    | 0.63580                         | 0.63159                         | 0.63095              | 0.68600            | 0.68600            | 0.68888            | 0.68600            | 0.68888            | 0.68888            |

Table 15.29. The MO to HO intercept geometrical bond parameters of branched-chain alkyl fluorides.  $R, R', R''$  are H or alkyl groups.  $E_{\sigma}$  is  $E_{\sigma}(\text{atom} - \text{atom}, \text{mvp}, \text{AO})$ .

| Bond                            | Atom           | $E_{\sigma}$<br>(eV)<br>Bond 1 | $i_{\sigma}$<br>(eV)<br>Bond 2 | $E_{\sigma}$<br>(eV)<br>Bond 3 | $E_{\sigma}$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>(eV) | $r_{\text{final}}$<br>(Å) | $E_{\text{final}}$<br>(eV)<br>Final | $\theta'$<br>(°) | $\theta_1$<br>(°) | $\theta_2$<br>(°) | $d_1$<br>(Å) | $d_2$<br>(Å) |
|---------------------------------|----------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|-------------------------------|---------------------------|-------------------------------------|------------------|-------------------|-------------------|--------------|--------------|
| $H_1-C_1-F_1$<br>(C-F (i))      | C <sub>1</sub> | -1.34946                       | 0                              | 0                              | 0                              | -152.96515                    | 0.91771                   | -16.17521                           | 100.77           | 79.23             | 47.86             | 1.15488      | 0.15714      |
| $H_1-C_1-F_1$<br>(C-F (ii))     | F <sub>1</sub> | -1.34946                       | 0                              | 0                              | 0                              | -152.96515                    | 0.91771                   | -16.17521                           | 100.77           | 79.23             | 47.86             | 1.15488      | 0.15714      |
| $H_1-C_1-F_1$<br>(C-F (iii))    | C <sub>1</sub> | -1.34946                       | -0.92918                       | 0                              | 0                              | -153.89433                    | 0.91771                   | -17.10440                           | 97.02            | 82.98             | 45.11             | 1.21483      | 0.09718      |
| $H_1-C_1-F_1$<br>(C-F (iv))     | F <sub>1</sub> | -1.34946                       | 0                              | 0                              | 0                              | -152.96515                    | 0.91771                   | -16.17521                           | 100.77           | 79.23             | 47.86             | 1.15488      | 0.15714      |
| $C_1-H_1$<br>(CH <sub>3</sub> ) | C <sub>1</sub> | -0.92918                       | 0                              | 0                              | 0                              | -152.34487                    | 0.91771                   | -15.56407                           | 77.49            | 102.51            | 41.48             | 1.23564      | 0.18708      |
| $C_1-H_1$<br>(CH <sub>2</sub> ) | C <sub>1</sub> | -0.92918                       | -0.92918                       | 0                              | 0                              | -153.47406                    | 0.91771                   | -16.68412                           | 68.47            | 111.53            | 35.84             | 1.35486      | 0.29933      |
| $C_1-H_1$<br>(CH)               | C <sub>1</sub> | -0.92918                       | -0.92918                       | -0.92918                       | 0                              | -154.40324                    | 0.91771                   | -17.61330                           | 61.10            | 118.90            | 31.37             | 1.42988      | 0.37326      |
| $H_1-C_1-H_1$<br>(C-C (a))      | C <sub>1</sub> | -0.92918                       | 0                              | 0                              | 0                              | -152.54487                    | 0.91771                   | -15.56407                           | 63.82            | 116.18            | 30.08             | 1.33879      | 0.33106      |
| $H_1-C_1-H_1$<br>(C-C (b))      | C <sub>1</sub> | -0.92918                       | -0.92918                       | 0                              | 0                              | -153.47406                    | 0.91771                   | -16.68412                           | 56.41            | 123.59            | 26.06             | 1.90890      | 0.45117      |
| $R-H_1-C_1$<br>(C-C (c))        | C <sub>1</sub> | -0.92918                       | -0.92918                       | -0.92918                       | 0                              | -154.40324                    | 0.91771                   | -17.61330                           | 48.30            | 131.70            | 21.90             | 1.97162      | 0.51388      |
| $R-H_1-C_1$<br>(C-C (d))        | C <sub>1</sub> | -0.92918                       | -0.92918                       | -0.92918                       | -0.72457                       | -154.71860                    | 0.91771                   | -17.92866                           | 48.21            | 131.79            | 21.74             | 1.95734      | 0.50570      |
| $R-H_1-C_1$<br>(C-C (e))        | C <sub>1</sub> | -0.92918                       | -0.92918                       | -0.92918                       | 0                              | -154.40324                    | 0.91771                   | -17.61330                           | 48.30            | 131.70            | 21.90             | 1.97162      | 0.51388      |
| $R-H_1-C_1$<br>(C-C (f))        | C <sub>1</sub> | -0.92918                       | -0.92918                       | -0.92918                       | -0.72457                       | -154.71860                    | 0.91771                   | -17.92866                           | 50.04            | 129.96            | 22.66             | 1.94462      | 0.49298      |
| $R-H_1-C_1$<br>(C-C (g))        | C <sub>1</sub> | -0.92918                       | -0.92918                       | -0.92918                       | 0                              | -154.40324                    | 0.91771                   | -17.61330                           | 52.78            | 127.22            | 24.04             | 1.92443      | 0.47279      |
| $R-H_1-C_1$<br>(C-C (h))        | C <sub>1</sub> | -0.92918                       | -0.92918                       | -0.92918                       | -0.72457                       | -154.71860                    | 0.91771                   | -17.92866                           | 50.04            | 129.96            | 22.66             | 1.94462      | 0.49298      |



Table 15.30. The energy parameters (eV) of functional groups of branched-chain alkyl fluorides.

| Parameters                       | C-F (i) Group | C-F (ii) Group | CH <sub>3</sub> Group | CH <sub>2</sub> Group | C-H Group | C-C (a) Group | C-C (b) Group | C-C (c) Group | C-C (d) Group | C-C (e) Group | C-C (f) Group |
|----------------------------------|---------------|----------------|-----------------------|-----------------------|-----------|---------------|---------------|---------------|---------------|---------------|---------------|
| $n_1$                            | 1             | 1              | 3                     | 2                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $n_2$                            | 0             | 0              | 2                     | 1                     | 0         | 0             | 0             | 0             | 0             | 0             | 0             |
| $n_3$                            | 0             | 0              | 0                     | 0                     | 0         | 0             | 0             | 0             | 0             | 0             | 0             |
| $C_1$                            | 0.5           | 0.5            | 0.75                  | 0.75                  | 0.75      | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           |
| $C_2$                            | 1             | 1              | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_3$                            | 1             | 1              | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_4$                            | 0.77087       | 0.77087        | 0.91771               | 0.91771               | 0.91771   | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       |
| $C_5$                            | 0             | 0              | 0                     | 0                     | 0         | 0             | 0             | 0             | 0             | 0             | 0             |
| $C_6$                            | 2             | 2              | 1                     | 1                     | 1         | 2             | 2             | 2             | 2             | 2             | 2             |
| $C_7$                            | 0             | 0              | 3                     | 2                     | 1         | 0             | 0             | 0             | 0             | 0             | 0             |
| $C_{10}$                         | 0.5           | 0.5            | 0.75                  | 0.75                  | 0.75      | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           |
| $C_{10}$                         | 1             | 1              | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $V_1$ (eV)                       | -32.02108     | -32.02108      | -107.32728            | -70.41425             | -35.12015 | -28.79214     | -28.79214     | -29.10112     | -28.79214     | -29.10112     | -29.10112     |
| $V_2$ (eV)                       | 10.37015      | 10.37015       | 38.92728              | 25.78002              | 12.87680  | 9.3352        | 9.3352        | 9.37273       | 9.3352        | 9.37273       | 9.37273       |
| $V_3$ (eV)                       | 9.30097       | 9.30097        | 32.53914              | 21.06675              | 10.48582  | 6.77464       | 6.77464       | 6.90500       | 6.77464       | 6.90500       | 6.90500       |
| $V_4$ (eV)                       | -4.65048      | -4.65048       | -16.26957             | -10.53337             | -3.24291  | -3.38732      | -3.38732      | -3.45250      | -3.38732      | -3.45250      | -3.45250      |
| $E_{10}$ (eV)                    | -14.63489     | -14.63489      | -15.56407             | -15.56407             | -14.63489 | -15.56407     | -15.56407     | -15.35946     | -15.56407     | -15.35946     | -15.35946     |
| $\Delta E_{10,100}$ (eV)         | 0             | 0              | 0                     | 0                     | 0         | 0             | 0             | 0             | 0             | 0             | 0             |
| $E_{10}$ (eV)                    | -14.63489     | -14.63489      | -15.56407             | -15.56407             | -14.63489 | -15.56407     | -15.56407     | -15.35946     | -15.56407     | -15.35946     | -15.35946     |
| $E_{10}$ (eV)                    | -31.63534     | -31.63534      | -67.69451             | -49.66493             | -31.63533 | -31.63537     | -31.63537     | -31.63535     | -31.63537     | -31.63535     | -31.63535     |
| $E_{10}$ (eV)                    | -2.69802      | -2.69802       | 0                     | 0                     | 0         | -1.85836      | -1.85836      | -1.44915      | -1.85836      | -1.44915      | -1.44915      |
| $\omega$ (10 <sup>5</sup> rad/s) | -34.33429     | -34.33429      | -67.69450             | -49.66493             | -31.63537 | -33.49373     | -33.49373     | -33.08452     | -33.49373     | -33.08452     | -33.08452     |
| $E_{10}$ (eV)                    | 24.8506       | 24.8506        | 24.9286               | 24.2751               | 24.1759   | 9.43699       | 9.43699       | 15.4846       | 9.43699       | 9.55643       | 9.55643       |
| $E_{10}$ (eV)                    | 16.35707      | 16.35707       | 16.40846              | 15.97831              | 15.91299  | 6.21159       | 6.21159       | 10.19220      | 6.21159       | 6.29021       | 6.29021       |
| $E_{10}$ (eV)                    | -0.27472      | -0.27472       | -0.25352              | -0.25017              | -0.24966  | -0.16515      | -0.16515      | -0.20896      | -0.16515      | -0.16416      | -0.16416      |
| $E_{10}$ (eV)                    | 0.13849       | 0.10911        | 0.35532               | 0.35532               | 0.35532   | 0.12312       | 0.17978       | 0.09944       | 0.12312       | 0.12312       | 0.12312       |
| $E_{10}$ (eV)                    | -0.20547      | -0.14371       | -0.22757              | -0.14502              | -0.07200  | -0.10359      | -0.07526      | -0.15924      | -0.10359      | -0.10260      | -0.10260      |
| $E_{10}$ (eV)                    | 0.14803       | 0.14803        | 0.14803               | 0.14803               | 0.14803   | 0.14803       | 0.14803       | 0.14803       | 0.14803       | 0.14803       | 0.14803       |
| $E_{10}$ (eV)                    | -34.53976     | -34.47800      | -67.92207             | -49.80996             | -31.70737 | -33.59732     | -33.49373     | -33.24376     | -33.59732     | -33.18712     | -33.18712     |
| $E_{10}$ (eV)                    | -14.63489     | -14.63489      | -14.63489             | -14.63489             | -14.63489 | -14.63489     | -14.63489     | -14.63489     | -14.63489     | -14.63489     | -14.63489     |
| $E_{10}$ (eV)                    | 0             | 0              | -13.59844             | -13.59844             | -13.59844 | 0             | 0             | 0             | 0             | 0             | 0             |
| $E_{10}$ (eV)                    | 5.26998       | 5.20822        | 12.49186              | 7.83016               | 3.32601   | 4.32754       | 4.29921       | 3.97398       | 4.17951       | 3.62128       | 3.91734       |

Table 15.31. The total bond energies of branched-chain alkyl fluorides calculated using the functional group composition and the energies of Table 15.30 compared to the experimental values [2]. The magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_{10}$  values based on composition is given by (15.58).

| Formula                         | Name               | C-F (i) | C-F (ii) | CH <sub>3</sub> | CH <sub>2</sub> | CH | C-C (a) | C-C (b) | C-C (c) | C-C (d) | C-C (e) | C-C (f) | $E_{mag}$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---------------------------------|--------------------|---------|----------|-----------------|-----------------|----|---------|---------|---------|---------|---------|---------|-----------|-----------------------------------|-------------------------------------|----------------|
| CF <sub>4</sub>                 | Tetrafluoromethane | 4       | 0        | 0               | 0               | 0  | 0       | 0       | 0       | 0       | 0       | 0       | 0         | 21.07992                          | 21.016                              | -0.00303       |
| CHF <sub>3</sub>                | Trifluoromethane   | 3       | 0        | 0               | 0               | 1  | 0       | 0       | 0       | 0       | 0       | 0       | 1         | 19.28398                          | 19.362                              | 0.00405        |
| CH <sub>2</sub> F <sub>2</sub>  | Diffuoromethane    | 2       | 0        | 0               | 1               | 0  | 0       | 0       | 0       | 0       | 0       | 0       | 0         | 18.37012                          | 18.280                              | -0.00496       |
| C <sub>2</sub> H <sub>5</sub> F | 1-Fluoropropane    | 0       | 1        | 1               | 2               | 0  | 0       | 0       | 0       | 0       | 0       | 0       | -1        | 41.86745                          | 41.885                              | 0.00041        |
| C <sub>3</sub> H <sub>7</sub> F | 2-Fluoropropane    | 0       | 1        | 2               | 0               | 1  | 0       | 0       | 0       | 0       | 0       | 0       | -1        | 41.96834                          | 41.963                              | -0.00012       |



# ALKYL CHLORIDES ( $C_n H_{2n+2-m} Cl_m$ , $n=1,2,3,4,5\ldots\infty$ $m=1,2,3\ldots\infty$ )

The branched-chain alkyl chlorides,  $C_n H_{2n+2-m} Cl_m$ , may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds wherein at least one  $H$  is replaced by a chlorine. The  $C-Cl$  bond comprises a functional group for each case of  $Cl$  replacing a  $H$  of methane for the series  $H_{4-m}C-Cl_m$ ,  $m=1,2,3$ , with the  $C-Cl$  bond of  $CCl_4$  comprising another functional group due to the limitation of the minimum energy of  $Cl$  matched to that of the  $C2sp^3$  HO. In addition, the  $C-Cl$  bond due to  $Cl$  replacing a  $H$  of an alkane is a function group. The methyl, methylene, methylene functional groups are equivalent to those of branched-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the  $C-Cl$  functional groups comprises the hybridization of the  $2s$  and  $2p$  AOs of each  $C$  to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the  $Cl$  AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl chlorides, the energy of chlorine is less than the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). Thus,  $c_2$  in Eq. (15.52) is one, and the energy matching condition is determined by the  $C_2$  parameter. Then,  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)), and the  $Cl$  AO has an energy of  $E(Cl) = -12.96764 \text{ eV}$ . To meet the equipotential condition of the union of the  $C-Cl$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $C_2$  of Eq. (15.52) for the  $C-Cl$ -bond MO given by Eqs. (15.68) and (15.70) is

$$C_2(C2sp^3HO \text{ to } Cl) = \frac{E(Cl)}{E(C, 2sp^3)} c_2(C2sp^3HO) = \frac{-12.96764 \text{ eV}}{-14.63489 \text{ eV}} (0.91771) = 0.81317 \quad (15.110)$$

The valence energy of the carbon  $2p$  is  $-11.2603 \text{ eV}$  and that of the  $Cl$  AO is  $-12.96764 \text{ eV}$ .

The energy difference is more than that of  $2E_r(C-C, 2sp^3)$  given by Eq. (14.151) for a single

bond. Thus,  $E_r(\text{atom} - \text{atom}, msp^3.AO)$  of the  $C - Cl$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $Cl$  atoms to the MO is  $-1.44915 \text{ eV}$  based on the energy match between the  $C2sp^3$  HO and the  $Cl$  AO corresponding to the energy contributions equivalent to those of methyl groups,  $-0.72457 \text{ eV}$  (Eq. (14.151)).

- 5 The symbols of the functional groups of branched-chain alkyl chlorides are given in Table 15.33. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl chlorides are given in Tables 15.34, 15.35, and 15.36, respectively. The total energy of each branched-chain alkyl chloride given in Table 15.37 was calculated as the sum over the integer multiple of each
- 10  $E_D(\text{Group})$  of Table 15.36 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that was subtracted from the weighted sum of the  $E_D(\text{Group})$  ( $\text{eV}$ ) values based on composition is given by Eq. (15.58). The  $C - C$  bonds to the  $CHCl$  group (one  $H$  bond to  $C$ ) were each treated as an iso  $C - C$  bond. The  $C - C$  bonds to the  $CCl$  group (no  $H$  bonds to  $C$ ) were
- 15 each treated as a tert-butyl  $C - C$ .  $E_{mag}$  was subtracted for each t-butyl group. The bond angle parameters of branched-chain alkyl chlorides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.111) are given in Table 15.38.

Table 15.33. The symbols of functional groups of branched-chain alkyl chlorides.

| Functional Group             | Group Symbol       |
|------------------------------|--------------------|
| CCl of $CCl_m H_{4-m}$       | $C - Cl$ (i)       |
| CCl of $CCl_4$               | $C - Cl$ (ii)      |
| CCl of $C_n H_{2n+2-m} Cl_m$ | $C - Cl$ (iii)     |
| $CH_3$ group                 | $C - H$ ( $CH_3$ ) |
| $CH_2$ group                 | $C - H$ ( $CH_2$ ) |
| CH                           | $C - H$            |
| CC bond (n-C)                | $C - C$ (a)        |
| CC bond (iso-C)              | $C - C$ (b)        |
| CC bond (tert-C)             | $C - C$ (c)        |
| CC (iso to iso-C)            | $C - C$ (d)        |
| CC (t to t-C)                | $C - C$ (e)        |
| CC (t to iso-C)              | $C - C$ (f)        |

Table 15.34. The geometrical bond parameters of branched-chain alkyl chlorides and experimental values [1].

Table 15.34. The geometrical bond parameters of branched-chain alkyl chlorides and experimental values [1].

| Parameter                             | $C-Cl$ (i)<br>Group        | $C-Cl$ (ii)<br>Group            | $C-Cl$ (iii)<br>Group                                      | $C-H$ ( $CH_3$ )<br>Group                             | $C-H$ ( $CH_2$ )<br>Group                             | $C-C$ (a)<br>Group   | $C-C$ (b)<br>Group                      | $C-C$ (c)<br>Group                      | $C-C$ (d)<br>Group                      | $C-C$ (e)<br>Group                      | $C-C$ (f)<br>Group                      |
|---------------------------------------|----------------------------|---------------------------------|------------------------------------------------------------|-------------------------------------------------------|-------------------------------------------------------|----------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|
| $\alpha$ ( $a_n$ )                    | 2.32621                    | 2.37026                         | 2.32621                                                    | 1.64920                                               | 1.67122                                               | 1.67465              | 2.12499                                 | 2.10725                                 | 2.12499                                 | 2.10725                                 | 2.10725                                 |
| $c'$ ( $a_n$ )                        | 1.69136                    | 1.70729                         | 1.69136                                                    | 1.04856                                               | 1.05553                                               | 1.05661              | 1.45744                                 | 1.45164                                 | 1.45744                                 | 1.45164                                 | 1.45164                                 |
| Bond Length<br>$2c'$ ( $\text{\AA}$ ) | 1.79005                    | 1.80692                         | 1.79005                                                    | 1.10974                                               | 1.11713                                               | 1.11827              | 1.54280                                 | 1.53635                                 | 1.54280                                 | 1.53635                                 | 1.53635                                 |
| Exp. Bond Length<br>( $\text{\AA}$ )  | 1.785<br>(methyl chloride) | 1.767<br>(carbon tetrachloride) | 1.802<br>(ethyl chloride)<br>1.790<br>(1,2-dichloroethane) | 1.107<br>( $C-H$ propane)<br>1.117<br>( $C-H$ butane) | 1.107<br>( $C-H$ propane)<br>1.117<br>( $C-H$ butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $h_c$ ( $a_n$ )                       | 1.59703                    | 1.64416                         | 1.59703                                                    | 1.27295                                               | 1.29569                                               | 1.29924              | 1.54616                                 | 1.52750                                 | 1.54616                                 | 1.52750                                 | 1.52750                                 |
|                                       | 0.72709                    | 0.72030                         | 0.72709                                                    | 0.63380                                               | 0.63159                                               | 0.63095              | 0.63600                                 | 0.63888                                 | 0.63600                                 | 0.63888                                 | 0.63888                                 |

Table 15.35. The MO to HO intercept geometrical bond parameters of branched-chain alkyl chlorides.  $R, R', R''$  are H or alkyl groups.  $E_T = E_T(\text{atom} - \text{atom}, \text{msp}^3, AC)$ .

| Bond                                               | Atom  | $E_T$<br>(eV)<br>Bond 1 | $E_T$<br>(eV)<br>Bond 2 | $E_T$<br>(eV)<br>Bond 3 | $E_T$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>( $\times 2sp^3$ )<br>(eV) | $r_{\text{calculated}}$<br>( $a_0$ ) | $r_{\text{final}}$<br>( $a_0$ ) | $E_{\text{calculated}}$<br>(eV)<br>Final | $E(C2sp^3)$<br>Final | $\theta^*$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | $d_1$<br>( $a_0$ ) | $d_2$<br>( $a_0$ ) |
|----------------------------------------------------|-------|-------------------------|-------------------------|-------------------------|-------------------------|-----------------------------------------------------|--------------------------------------|---------------------------------|------------------------------------------|----------------------|----------------------------|----------------------------|----------------------------|--------------------|--------------------|
| $H_{1m}-C^m-C^m$ , $m=1,2,3$<br>( $C^m-C^1$ (ii))  | $C^m$ | -0.72457                | 0                       | 0                       | 0                       | -152.24026                                          | 0.91771                              | 0.87495                         | -15.55033                                | -15.33946            | 69.62                      | 110.38                     | 30.90                      | 1.99599            | 0.30463            |
| $H_{1m}-C^m-C^m$ , $m=1,2,3$<br>( $C^m-C^1$ (ii))  | $C^1$ | -0.72457                | 0                       | 0                       | 0                       | -152.24026                                          | 1.05158                              | 0.87495                         | -15.55033                                | -15.33946            | 69.62                      | 110.38                     | 30.90                      | 1.99599            | 0.30463            |
| $C^m-C^1$<br>( $C^m-C^1$ (iii))                    | $C^m$ | -0.46459                | 0                       | 0                       | 0                       | -152.08028                                          | 0.91771                              | 0.88983                         | -15.29034                                | -15.09948            | 66.98                      | 115.02                     | 29.87                      | 2.05530            | 0.34801            |
| $C^m-C^1$<br>( $C^m-C^1$ (iii))                    | $C^1$ | -0.46459                | 0                       | 0                       | 0                       | -152.08028                                          | 1.05158                              | 0.88983                         | -15.29034                                | -15.09948            | 66.98                      | 115.02                     | 29.87                      | 2.05530            | 0.34801            |
| $H_{1m}-C^m-C^m$ , $m=1,2,3$<br>( $C^m-C^1$ (iii)) | $C^m$ | -0.72457                | -0.92918                | 0                       | 0                       | -153.26945                                          | 0.91771                              | 0.82562                         | -16.47951                                | -16.28864            | 63.18                      | 116.82                     | 27.48                      | 2.66384            | 0.37248            |
| $H_{1m}-C^m-C^m$ , $m=1,2,3$<br>( $C^m-C^1$ (iii)) | $C^1$ | -0.72457                | -0.92918                | 0                       | 0                       | -153.26945                                          | 1.05158                              | 0.87495                         | -15.55033                                | -15.33946            | 69.62                      | 110.38                     | 30.90                      | 1.99599            | 0.30463            |
| $C^m-H$ ( $H_3$ )<br>( $C^m-C^1$ (iii))            | $C^m$ | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                          | 0.91771                              | 0.86359                         | -15.75493                                | -15.56407            | 77.49                      | 102.51                     | 41.48                      | 1.23564            | 0.18708            |
| $C^m-H$ ( $H_3$ )<br>( $C^m-C^1$ (iii))            | $C^1$ | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                          | 0.91771                              | 0.81549                         | -16.68412                                | -16.49325            | 68.47                      | 111.53                     | 35.84                      | 1.35486            | 0.20933            |
| $C^m-H$ ( $H_3$ )<br>( $C^m-C^1$ (iii))            | $C^1$ | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                          | 0.91771                              | 0.77247                         | -17.61330                                | -17.42244            | 61.10                      | 118.90                     | 31.37                      | 1.42988            | 0.37326            |
| $H_3-C^m-C^m$ , $m=1,2,3$<br>( $C^m-C^1$ (iv))     | $C^m$ | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                          | 0.91771                              | 0.86359                         | -15.75493                                | -15.56407            | 63.82                      | 116.18                     | 30.08                      | 1.83879            | 0.38106            |
| $H_3-C^m-C^m$ , $m=1,2,3$<br>( $C^m-C^1$ (iv))     | $C^1$ | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                          | 0.91771                              | 0.81549                         | -16.68412                                | -16.49325            | 56.41                      | 123.59                     | 26.06                      | 1.90890            | 0.43117            |
| $R-H_3-C^m(H_3-C^m-C^m)$<br>( $C^m-C^1$ (v))       | $C^m$ | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                          | 0.91771                              | 0.77247                         | -17.61330                                | -17.42244            | 48.30                      | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| $R-H_3-C^m(H_3-C^m-C^m)$<br>( $C^m-C^1$ (v))       | $C^1$ | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -154.71860                                          | 0.91771                              | 0.75889                         | -17.92866                                | -17.73779            | 48.21                      | 131.79                     | 21.74                      | 1.95734            | 0.50570            |
| $isoC^m-C^m(H_3-C^m-C^m)$<br>( $C^m-C^1$ (vi))     | $C^m$ | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                          | 0.91771                              | 0.77247                         | -17.61330                                | -17.42244            | 48.30                      | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| $isoC^m-C^m(H_3-C^m-C^m)$<br>( $C^m-C^1$ (vi))     | $C^1$ | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -154.51399                                          | 0.91771                              | 0.76765                         | -17.92866                                | -17.73779            | 50.04                      | 129.96                     | 22.66                      | 1.94462            | 0.49298            |
| $isoC^m-C^m(H_3-C^m-C^m)$<br>( $C^m-C^1$ (vi))     | $C^m$ | -0.72457                | -0.92918                | -0.92918                | 0                       | -154.19863                                          | 0.91771                              | 0.78155                         | -17.40869                                | -17.21783            | 52.78                      | 127.22                     | 24.04                      | 1.92443            | 0.47279            |
| $isoC^m-C^m(H_3-C^m-C^m)$<br>( $C^m-C^1$ (vi))     | $C^1$ | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.51399                                          | 0.91771                              | 0.76765                         | -17.92866                                | -17.73779            | 50.04                      | 129.96                     | 22.66                      | 1.94462            | 0.49298            |

Table 15.36. The energy parameters (eV) of functional groups of branched-chain alkyl chlorides.

| Parameters                           | C-Cl<br>(i)<br>Group | C-Cl<br>(ii)<br>Group | C-Cl<br>(iii)<br>Group | CH <sub>3</sub><br>Group | CH <sub>2</sub><br>Group | C-H<br>Group | C-C (a)<br>Group | C-C (b)<br>Group | C-C (c)<br>Group | C-C (d)<br>Group | C-C (e)<br>Group | C-C (f)<br>Group |
|--------------------------------------|----------------------|-----------------------|------------------------|--------------------------|--------------------------|--------------|------------------|------------------|------------------|------------------|------------------|------------------|
| $\eta_1$                             | 1                    | 1                     | 1                      | 3                        | 2                        | 1            | 1                | 1                | 1                | 1                | 1                | 1                |
| $\eta_2$                             | 0                    | 0                     | 0                      | 2                        | 1                        | 0            | 0                | 0                | 0                | 0                | 0                | 0                |
| $\eta_3$                             | 0                    | 0                     | 0                      | 0                        | 0                        | 0            | 0                | 0                | 0                | 0                | 0                | 0                |
| $\zeta_1$                            | 0.5                  | 0.5                   | 0.5                    | 0.75                     | 0.75                     | 0.75         | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              |
| $\zeta_2$                            | 0.81317              | 0.81317               | 0.81317                | 1                        | 1                        | 1            | 1                | 1                | 1                | 1                | 1                | 1                |
| $\zeta_3$                            | 1                    | 1                     | 1                      | 1                        | 1                        | 1            | 1                | 1                | 1                | 1                | 1                | 1                |
| $\zeta_4$                            | 1                    | 1                     | 1                      | 0                        | 1                        | 1            | 0                | 0                | 0                | 1                | 1                | 0.91771          |
| $\zeta_5$                            | 2                    | 2                     | 2                      | 1                        | 1                        | 1            | 2                | 2                | 2                | 2                | 2                | 2                |
| $\zeta_6$                            | 0                    | 0                     | 0                      | 3                        | 2                        | 1            | 0                | 0                | 0                | 0                | 0                | 0                |
| $\zeta_{10}$                         | 0.5                  | 0.5                   | 0.5                    | 0.75                     | 0.75                     | 0.75         | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              |
| $\zeta_{20}$                         | 0.81317              | 0.81317               | 0.81317                | 1                        | 1                        | 1            | 1                | 1                | 1                | 1                | 1                | 1                |
| $\nu_1$ (eV)                         | -29.68411            | -28.95265             | -29.68411              | -107.32728               | -70.41425                | -35.12015    | -28.79214        | -28.79214        | -29.10112        | -28.79214        | -29.10112        | -29.10112        |
| $\nu_2$ (eV)                         | 8.04432              | 7.96922               | 8.04432                | 38.92728                 | 25.78002                 | 12.87680     | 9.33352          | 9.33352          | 9.37273          | 9.33352          | 9.37273          | 9.37273          |
| $\nu_3$ (eV)                         | 6.38036              | 6.10748               | 6.38036                | 32.53914                 | 21.06675                 | 10.48382     | 6.77464          | 6.77464          | 6.90500          | 6.77464          | 6.90500          | 6.90500          |
| $\nu_4$ (eV)                         | -3.19018             | -3.05374              | -3.19018               | -16.26957                | -10.53337                | -5.24291     | -3.38732         | -3.38732         | -3.45250         | -3.38732         | -3.45250         | -3.45250         |
| $\nu_5$ (eV)                         | -14.63489            | -14.63489             | -14.63489              | -15.56407                | -15.56407                | -14.63489    | -15.56407        | -15.56407        | -15.55946        | -15.56407        | -15.55946        | -15.55946        |
| $\Delta E_{12,10}^{\text{max}}$ (eV) | -1.44915             | -0.92918              | -1.44915               | 0                        | 0                        | 0            | 0                | 0                | 0                | 0                | 0                | 0                |
| $\nu_7$ (eV)                         | -13.18574            | -13.70571             | -13.18574              | -15.56407                | -15.56407                | -14.63489    | -15.56407        | -15.56407        | -15.55946        | -15.56407        | -15.55946        | -15.55946        |
| $\nu_8$ (eV)                         | -31.63536            | -31.63540             | -31.63536              | -67.69451                | -49.66493                | -31.63533    | -31.63537        | -31.63537        | -31.63533        | -31.63537        | -31.63533        | -31.63533        |
| $\nu_9$ (eV)                         | -1.44915             | -0.92918              | -1.44915               | 0                        | 0                        | 0            | -1.85836         | -1.85836         | -1.44915         | -1.85836         | -1.44915         | -1.44915         |
| $\nu_{12}$ (eV)                      | -33.08452            | -32.56455             | -33.08452              | -67.69450                | -49.66493                | -31.63537    | -33.49373        | -33.49373        | -33.08452        | -33.49373        | -33.08452        | -33.08452        |
| $\omega$ ( $10^{15}$ rad/s)          | 7.42995              | 7.22380               | 13.0612                | 24.9286                  | 24.2751                  | 24.1759      | 9.43699          | 9.43699          | 15.4846          | 9.43699          | 9.55643          | 9.55643          |
| $E_1$ (eV)                           | 4.89052              | 4.75483               | 8.59708                | 16.40846                 | 15.97831                 | 15.91299     | 6.21159          | 6.21159          | 10.19220         | 6.21159          | 6.29021          | 6.29021          |
| $E_2$ (eV)                           | -0.14475             | -0.14048              | -0.19191               | -0.25352                 | -0.25017                 | -0.24966     | -0.16515         | -0.16515         | -0.20896         | -0.16515         | -0.16416         | -0.16416         |
| $E_3$ (eV)                           | 0.08059              | 0.08059               | 0.09113                | 0.35532                  | 0.35532                  | 0.35532      | 0.12312          | 0.12312          | 0.09944          | 0.12312          | 0.12312          | 0.12312          |
| $E_4$ (eV)                           | -0.10445             | -0.10019              | -0.14635               | -0.22757                 | -0.14502                 | -0.07200     | -0.10359         | -0.07526         | -0.15924         | -0.10359         | -0.10260         | -0.10260         |
| $E_{100}$ (eV)                       | 0.14803              | 0.14803               | 0.14803                | 0.14803                  | 0.14803                  | 0.14803      | 0.14803          | 0.14803          | 0.14803          | 0.14803          | 0.14803          | 0.14803          |
| $E_7$ (eV)                           | -33.18897            | -32.66473             | -33.23086              | -67.92207                | -49.80996                | -31.70737    | -33.59732        | -33.49373        | -33.24376        | -33.59732        | -33.18712        | -33.18712        |
| $E_{1000}$ (eV)                      | -14.63489            | -14.63489             | -14.63489              | -14.63489                | -14.63489                | -14.63489    | -14.63489        | -14.63489        | -14.63489        | -14.63489        | -14.63489        | -14.63489        |
| $E_{10000}$ (eV)                     | 0                    | 0                     | 0                      | -13.59844                | -13.59844                | -13.59844    | 0                | 0                | 0                | 0                | 0                | 0                |
| $F_{11}$ (eV)                        | 3.77116              | 3.39496               | 3.96108                | 12.49186                 | 7.83016                  | 3.32601      | 4.32754          | 4.29921          | 3.97398          | 4.17951          | 3.62128          | 3.91734          |

Table 15.37. The total bond energies of branched-chain alkyl chlorides calculated using the functional group composition and the energies of Table 15.36 compared to the experimental values [2]. The magnetic energy  $E_{ms}$  that is subtracted from the weighted sum of the  $E_{\sigma}(E_{\text{lower}})$  ( $eV$ ) values based on composition is given by (15.58).

| Formula                            | Name               | C-Cl (i) | C-Cl (ii) | C-Cl (iii) | CH <sub>3</sub> | CH <sub>2</sub> | CH (i) | CH (ii) | CH (iii) | C-C (a) | C-C (b) | C-C (c) | C-C (d) | C-C (e) | C-C (f) | $E_{ms}$ | Calculated Total Bond Energy (eV) | Experiment al Total Bond Energy (eV) | Relative Error |
|------------------------------------|--------------------|----------|-----------|------------|-----------------|-----------------|--------|---------|----------|---------|---------|---------|---------|---------|---------|----------|-----------------------------------|--------------------------------------|----------------|
| CCl <sub>4</sub>                   | Tetrachloromethane | 0        | 0         | 0          | 0               | 0               | 0      | 0       | 0        | 0       | 0       | 0       | 0       | 0       | 0       | -1       | 13.43181                          | 13.448                               | 0.00123        |
| CHCl <sub>3</sub>                  | Trichloromethane   | 3        | 0         | 0          | 0               | 0               | 1      | 0       | 0        | 0       | 0       | 0       | 0       | 0       | 0       | -1       | 14.49146                          | 14.523                               | 0.00217        |
| CH <sub>2</sub> Cl <sub>2</sub>    | Dichloromethane    | 2        | 0         | 0          | 0               | 1               | 0      | 0       | 0        | 0       | 0       | 0       | 0       | 0       | 0       | 0        | 15.37248                          | 15.450                               | 0.00499        |
| CH <sub>3</sub> Cl                 | Chloromethane      | 1        | 0         | 0          | 1               | 0               | 0      | 0       | 0        | 0       | 0       | 0       | 0       | 0       | 0       | 0        | 16.26302                          | 16.312                               | 0.00299        |
| C <sub>2</sub> H <sub>5</sub> Cl   | 1-Chloroethane     | 0        | 0         | 1          | 1               | 1               | 0      | 0       | 0        | 1       | 0       | 0       | 0       | 0       | 0       | 0        | 28.61064                          | 28.571                               | -0.00138       |
| C <sub>3</sub> H <sub>7</sub> Cl   | 1-Chloropropane    | 0        | 0         | 1          | 1               | 2               | 0      | 0       | 0        | 2       | 0       | 0       | 0       | 0       | 0       | 0        | 40.76834                          | 40.723                               | -0.00112       |
| C <sub>4</sub> H <sub>9</sub> Cl   | 1-Chlorobutane     | 0        | 0         | 1          | 1               | 3               | 0      | 0       | 0        | 3       | 0       | 0       | 0       | 0       | 0       | 0        | 52.92604                          | 52.858                               | -0.00028       |
| C <sub>5</sub> H <sub>11</sub> Cl  | 1-Chloropentane    | 0        | 0         | 1          | 1               | 4               | 0      | 0       | 0        | 4       | 0       | 0       | 0       | 0       | 0       | 0        | 65.08379                          | 65.061                               | -0.00037       |
| C <sub>6</sub> H <sub>13</sub> Cl  | 1-Chlorohexane     | 0        | 0         | 1          | 1               | 5               | 0      | 0       | 0        | 5       | 0       | 0       | 0       | 0       | 0       | 0        | 77.34233                          | 77.313                               | -0.00038       |
| C <sub>7</sub> H <sub>15</sub> Cl  | 1-Chloroheptane    | 0        | 0         | 1          | 1               | 6               | 0      | 0       | 0        | 6       | 0       | 0       | 0       | 0       | 0       | 0        | 89.60197                          | 89.584                               | -0.00038       |
| C <sub>8</sub> H <sub>17</sub> Cl  | 1-Chlorooctane     | 0        | 0         | 1          | 1               | 7               | 0      | 0       | 0        | 7       | 0       | 0       | 0       | 0       | 0       | 0        | 101.85984                         | 101.864                              | 0.00007        |
| C <sub>9</sub> H <sub>19</sub> Cl  | 1-Chlorononane     | 0        | 0         | 1          | 1               | 8               | 0      | 0       | 0        | 8       | 0       | 0       | 0       | 0       | 0       | 0        | 114.11971                         | 114.125                              | 0.00009        |
| C <sub>10</sub> H <sub>21</sub> Cl | 1-Chlorodecane     | 0        | 0         | 1          | 1               | 9               | 0      | 0       | 0        | 9       | 0       | 0       | 0       | 0       | 0       | 0        | 126.38058                         | 126.384                              | 0.00018        |

Table 15.38. The bond angle parameters of branched-chain alkyl chlorides and experimental values [1]. In the calculation of  $\theta_i$ , the parameters from the preceding angle were used.  $E_i$  is  $E_i(\text{atom} - \text{atom}, \text{mp}, \text{AO})$ .

| Atom of angle                                | $2c_1$<br>Bond 1<br>( $a_1$ ) | $2c_2$<br>Bond 2<br>( $a_2$ ) | $2c_3$<br>Terminal<br>Atom<br>( $a_3$ ) | $E_1$<br>Atom 1<br>Designation<br>(Table 15.3.A) | $E_2$<br>Atom 2<br>Designation<br>(Table 15.3.A) | $c_1$<br>Atom 1 | $c_2$<br>Atom 2 | $c_3$ | $C_1$                     | $C_2$ | $C_3$   | $\theta_i$<br>( $^\circ$ ) | $\theta_j$<br>( $^\circ$ ) | $\theta_k$<br>( $^\circ$ ) | Cal.<br>$\theta$<br>( $^\circ$ ) | Exp. $\theta$<br>( $^\circ$ )                   |
|----------------------------------------------|-------------------------------|-------------------------------|-----------------------------------------|--------------------------------------------------|--------------------------------------------------|-----------------|-----------------|-------|---------------------------|-------|---------|----------------------------|----------------------------|----------------------------|----------------------------------|-------------------------------------------------|
| $\angle C_1 C_2 C_3$<br>( $C_3 - C_1$ (iii)) | 3.36271                       | 3.36271                       | 5.3689                                  | -14.82575<br>$C_1$                               | -14.82575<br>$C_1$                               | 0.91771         | 0.91771         | 1     | 0.81317<br>(Eq. (15.111)) | 1     | 0.91771 | -0.92918                   |                            |                            | 111.40                           | 112.0<br>(dichloromethane)                      |
| $\angle H C_1 C_2$<br>( $C_3 - C_1$ (iii))   | 2.11106                       | 3.36271                       | 4.5961                                  | -16.27499<br>$C_3$                               | -12.96764<br>$C_1$                               | 0.83600         | 0.91771         | 0.75  | 0.9310<br>(Eq. (15.63))   | 0.75  | 1.09775 | 0                          |                            |                            | 111.46                           | 111.3<br>(chloroform)                           |
| $\angle H C_1 H$                             | 2.09711                       | 2.09711                       | 3.4252                                  | -15.75493                                        |                                                  | 0.86359         | 1               | 0.75  | 1                         | 1     | 1.15796 | 0                          |                            |                            | 109.50                           | 109.2<br>( $\angle H C_2 H$ adjacent to $C_2$ ) |
| $\angle C_1 C_2 C_3$<br>( $C_3 - C_1$ (iii)) | 2.91547                       | 3.36271                       | 5.1539                                  | -15.75493<br>$C_3$                               | -12.96764<br>$C_1$                               | 0.86359         | 0.86359         | 1     | 0.81317<br>(Eq. (15.111)) | 1     | 0.86359 | -0.92918                   |                            |                            | 109.61                           | 109.8<br>( $\angle H C_2 H$ adjacent to $C_2$ ) |
| $\angle C_1 C_2 H$<br>( $C_3 - C_1$ (iii))   | 2.91547                       | 2.11106                       | 4.1633                                  | -15.59033<br>$C_3$                               | -14.82575<br>$C_1$                               | 0.87495         | 0.91771         | 0.75  | 1                         | 0.75  | 1.04887 | 0                          |                            |                            | 110.83                           | 110.6<br>(ethyl chloride)                       |
| $\angle H C_1 H$                             | 2.11106                       | 2.11106                       | 3.4252                                  | -15.75493                                        |                                                  | 0.86359         | 1               | 0.75  | 1                         | 1     | 1.15796 | 0                          |                            |                            | 108.44                           | 107<br>(propane)                                |
| $\angle C_1 C_2 C_3$<br>( $C_3 - C_1$ (iii)) | 2.91547                       | 3.36271                       | 5.1539                                  | -15.75493<br>$C_3$                               | -12.96764<br>$C_1$                               | 0.86359         | 0.86359         | 1     | 0.81317<br>(Eq. (15.111)) | 1     | 0.86359 | -0.92918                   |                            |                            | 110.49                           | 112<br>(propane)                                |
| $\angle C_1 C_2 H$                           | 2.91547                       | 2.11106                       | 4.1633                                  | -15.59033<br>$C_3$                               | -14.82575<br>$C_1$                               | 0.87495         | 0.91771         | 0.75  | 1                         | 0.75  | 1.04887 | 0                          |                            |                            | 110.49                           | 113.8<br>(butane)                               |
| $\angle C_1 C_2 C_3$<br>( $C_3 - C_1$ (iii)) | 2.91547                       | 3.36271                       | 5.1539                                  | -15.75493<br>$C_3$                               | -12.96764<br>$C_1$                               | 0.86359         | 0.86359         | 1     | 0.81317<br>(Eq. (15.111)) | 1     | 0.86359 | -0.92918                   |                            |                            | 110.49                           | 110.8<br>(isobutane)                            |
| $\angle C_1 C_2 H$                           | 2.91547                       | 2.11106                       | 4.1633                                  | -15.59033<br>$C_3$                               | -14.82575<br>$C_1$                               | 0.87495         | 0.91771         | 0.75  | 1                         | 0.75  | 1.04887 | 0                          |                            |                            | 110.49                           | 111.0<br>(butane)                               |
| $\angle C_1 C_2 C_3$<br>( $C_3 - C_1$ (iii)) | 2.91547                       | 3.36271                       | 5.1539                                  | -15.75493<br>$C_3$                               | -12.96764<br>$C_1$                               | 0.86359         | 0.86359         | 1     | 0.81317<br>(Eq. (15.111)) | 1     | 0.86359 | -0.92918                   |                            |                            | 110.49                           | 111.4<br>(isobutane)                            |
| $\angle C_1 C_2 H$                           | 2.91547                       | 2.11106                       | 4.1633                                  | -15.59033<br>$C_3$                               | -14.82575<br>$C_1$                               | 0.87495         | 0.91771         | 0.75  | 1                         | 0.75  | 1.04887 | 0                          |                            |                            | 111.27                           | 111.4<br>(isobutane)                            |
| $\angle C_1 C_2 C_3$<br>( $C_3 - C_1$ (iii)) | 2.91547                       | 3.36271                       | 5.1539                                  | -15.75493<br>$C_3$                               | -12.96764<br>$C_1$                               | 0.86359         | 0.86359         | 1     | 0.81317<br>(Eq. (15.111)) | 1     | 0.86359 | -0.92918                   |                            |                            | 111.27                           | 111.4<br>(isobutane)                            |
| $\angle C_1 C_2 H$                           | 2.91547                       | 2.11106                       | 4.1633                                  | -15.59033<br>$C_3$                               | -14.82575<br>$C_1$                               | 0.87495         | 0.91771         | 0.75  | 1                         | 0.75  | 1.04887 | 0                          |                            |                            | 107.50                           | 107.50<br>(isobutane)                           |



# ALKYL BROMIDES ( $C_n H_{2n+2-m} Br_m$ , $n = 1, 2, 3, 4, 5 \dots \infty$ $m = 1, 2, 3 \dots \infty$ )

The branched-chain alkyl bromides,  $C_n H_{2n+2-m} Br_m$ , may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds wherein at least one  $H$  is replaced by a bromine. The  $C-Br$  bond comprises a functional group for each case of  $Br$  replacing a  $H$  of methane for the series  $H_{4-m} C-Br_m$ ,  $m = 1, 2, 3$ , with the  $C-Br$  bond of  $CBr_4$  comprising another functional group due to the limitation of the minimum energy of  $Br$  matched to that of the  $C2sp^3$  HO. In addition, the  $C-Br$  bond due to  $Br$  replacing a  $H$  of an alkane is a function group. The methyl, methylene, methylene functional groups are equivalent to those of branched-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2 CH$ ) and t-butyl ( $(CH_3)_3 C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the  $C-Br$  functional groups comprises the hybridization of the  $2s$  and  $2p$  shells of each  $C$  to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  hybridized orbital (HO) and the  $Br$  AO to form a molecular orbital (MO) permits each participating orbital to decrease in radius and energy. In alkyl bromides, the energy of bromine is less than the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). Thus,  $c_2$  in Eq. (15.52) is one, and the energy matching condition is determined by the  $C_2$  parameter. Then, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)), and the  $Br$  AO has an energy of  $E(Br) = -11.81381 \text{ eV}$ . To meet the equipotential condition of the union of the  $C-Br$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $C_2$  of Eq. (15.52) for the  $C-Br$ -bond MO given by Eqs. (15.68) and (15.70) is

$$C_2(C2sp^3 HO \text{ to } Br) = \frac{E(Br)}{E(C, 2sp^3)} c_2(C2sp^3 HO) = \frac{-11.81381 \text{ eV}}{-14.63489 \text{ eV}} (0.91771) = 0.74081 \quad (15.112)$$

The valence energy of the carbon  $2p$  is  $-11.2603 \text{ eV}$  and that of the  $Br$  AO is  $-11.81381 \text{ eV}$ . The energy difference is less than that of  $E_r(C-C, 2sp^3)$  given by Eq. (14.151) for a single bond. Thus,  $E_r(atom - atom, msp^3.AO)$  of the alkyl  $C-Br$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $Br$  atoms to the MO is  $-0.92918 \text{ eV}$  (Eq. (14.513) based on the maximum single-bond-energy contribution of the  $C2sp^3$  HO.  $E_r(atom - atom, msp^3.AO)$  of the series  $CBr_m H_{4-m}$ ,  $m=1,2,3$  is equivalent to those of methyl groups,  $-0.72457 \text{ eV}$  (Eq. (14.151)). For  $CBr_4$ ,  $E_r(atom - atom, msp^3.AO)$  of the  $C-Br$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $Br$  atoms to the MO is  $-0.36229 \text{ eV}$  (Eqs. (15.18-15.20 and Eq. (15.29) with a linear combination of  $s=1$ ,  $E_r(atom - atom, msp^3.AO) = -0.72457 \text{ eV}$  and  $E_r(atom - atom, msp^3.AO) = 0$ ) based on the maximum charge density on the  $C2sp^3$  HO.

The symbols of the functional groups of branched-chain alkyl bromides are given in Table 15.39. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl bromides are given in Tables 15.40, 15.41, and 15.42, respectively. The total energy of each branched-chain alkyl bromide given in Table 15.43 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.42 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that was subtracted from the weighted sum of the  $E_D(Group)$  ( $\text{eV}$ ) values based on composition is given by Eq. (15.58). The  $C-C$  bonds to the  $CHBr$  group (one  $H$  bond to  $C$ ) were each treated as an iso  $C-C$  bond. The  $C-C$  bonds to the  $CBr$  group (no  $H$  bonds to  $C$ ) were each treated as a tert-butyl  $C-C$ .  $E_{mag}$  is subtracted for each t-butyl group. In the case of 2,3-dibromo-2-methylbutane,  $E_{mag}$  is positive since the terms due to the two bromine atoms cancel that of the t-butyl and  $CH$  groups. The bond angle parameters of branched-chain alkyl bromides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.112) are given in Table 15.44.

Table 15.39. The symbols of functional groups of branched-chain alkyl bromides.

| Functional Group             | Group Symbol       |
|------------------------------|--------------------|
| CBr of $CB_r_m H_{4-m}$      | $C - Br$ (i)       |
| CBr of $CB_r_4$              | $C - Br$ (ii)      |
| CBr of $C_n H_{2n+2-m} Br_m$ | $C - Br$ (iii)     |
| $CH_3$ group                 | $C - H$ ( $CH_3$ ) |
| $CH_2$ group                 | $C - H$ ( $CH_2$ ) |
| CH                           | $C - H$            |
| CC bond (n-C)                | $C - C$ (a)        |
| CC bond (iso-C)              | $C - C$ (b)        |
| CC bond (tert-C)             | $C - C$ (c)        |
| CC (iso to iso-C)            | $C - C$ (d)        |
| CC (t to t-C)                | $C - C$ (e)        |
| CC (t to iso-C)              | $C - C$ (f)        |

Table 15.40. The geometrical bond parameters of branched-chain alkyl bromides and experimental values [1].

| Parameter                      | C-Br (i)<br>Group      | C-Br (ii)<br>Group          | C-Br (iii)<br>Group                                        | C-H (CH <sub>3</sub> )<br>Group                                 | C-H (CH <sub>2</sub> )<br>Group                                 | C-C (a)<br>Group  | C-C (b)<br>Group                  | C-C (c)<br>Group                  | C-C (d)<br>Group                  | C-C (e)<br>Group                  | C-C (f)<br>Group                  |
|--------------------------------|------------------------|-----------------------------|------------------------------------------------------------|-----------------------------------------------------------------|-----------------------------------------------------------------|-------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| $\alpha$ (°)                   | 2.49163                | 2.52309                     | 2.47329                                                    | 1.67122                                                         | 1.64920                                                         | 1.67465           | 2.12499                           | 2.10725                           | 2.12499                           | 2.10725                           | 2.10725                           |
| $\alpha'$ (°)                  | 1.83395                | 1.84622                     | 1.82719                                                    | 1.04856                                                         | 1.04856                                                         | 1.05661           | 1.45744                           | 1.45164                           | 1.45744                           | 1.45164                           | 1.45164                           |
| Bond Length<br>2c' (Å)         | 1.94097                | 1.95396                     | 1.93381                                                    | 1.10974                                                         | 1.10974                                                         | 1.11713           | 1.54280                           | 1.53635                           | 1.54280                           | 1.53635                           | 1.53635                           |
| Exp. Bond Length<br>Length (Å) | 1.953 (methyl bromide) | 1.955 (carbon tetrabromide) | 1.93 (1,1,1-tribromoethane)<br>1.950 (1,1,2-dibromoethane) | 1.107 (C-H propane)<br>1.117 (C-H butane)<br>1.117 (C-H butane) | 1.107 (C-H propane)<br>1.117 (C-H butane)<br>1.117 (C-H butane) | 1.122 (isobutane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) |
| $h_c$ (°)                      | 1.68667                | 1.72265                     | 1.66689                                                    | 1.27295                                                         | 1.27295                                                         | 1.29569           | 1.54616                           | 1.52750                           | 1.54616                           | 1.52750                           | 1.52750                           |
| $\epsilon$                     | 0.73604                | 0.73115                     | 0.73877                                                    | 0.63580                                                         | 0.63580                                                         | 0.63159           | 0.68600                           | 0.68888                           | 0.68600                           | 0.68888                           | 0.68888                           |

Table 15.41. The MO to HO intercept geometrical bond parameters of branched-chain alkyl bromides.  $R, R', R''$  are H or alkyl groups.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{msp}^2, \text{AO})$ .

| Bond                                                                                    | Atom | $E_T$<br>(eV)<br>Bond 1 | $E_T$<br>(eV)<br>Bond 2 | $E_T$<br>(eV)<br>Bond 3 | $E_T$<br>(eV)<br>Bond 4 | Final Total<br>Energy (2sp <sup>2</sup> )<br>(eV) | $r_{\text{final}}$<br>(a <sub>0</sub> ) | $r_{\text{final}}$<br>(a <sub>0</sub> ) | $E_{\text{redox}}$<br>(eV)<br>Final | $E(2sp^2)$<br>(eV)<br>Final | $\theta'$<br>(°) | $\theta_1$<br>(°) | $\theta_2$<br>(°) | $d_1$<br>(a <sub>0</sub> ) | $d_2$<br>(a <sub>0</sub> ) |
|-----------------------------------------------------------------------------------------|------|-------------------------|-------------------------|-------------------------|-------------------------|---------------------------------------------------|-----------------------------------------|-----------------------------------------|-------------------------------------|-----------------------------|------------------|-------------------|-------------------|----------------------------|----------------------------|
| $H_{\text{atom}}(C_{\text{atom}} - Br_{\text{atom}})$ , $m = 1, 2, 3$<br>(C-Br (i))     | C    | -0.36229                | 0                       | 0                       | 0                       | -151.97798                                        | 0.91771                                 | 0.89582                                 | -15.18804                           | -14.99717                   | 68.10            | 111.90            | 29.52             | 2.16808                    | 0.33415                    |
| $H_{\text{atom}}(C_{\text{atom}} - Br_{\text{atom}})$ , $m = 1, 2, 3$<br>(C-Br (ii))    | Br   | -0.36229                | 0                       | 0                       | 0                       | -151.97798                                        | 1.15169                                 | 0.89582                                 | -15.18804                           | -14.99717                   | 68.10            | 111.90            | 29.52             | 2.16808                    | 0.33415                    |
| $H_{\text{atom}}(C_{\text{atom}} - Br_{\text{atom}})$ , $m = 1, 2, 3$<br>(C-Br (iii))   | C    | -0.18114                | 0                       | 0                       | 0                       | -151.79683                                        | 0.91771                                 | 0.90664                                 | -15.00689                           | -14.81063                   | 66.10            | 113.90            | 28.76             | 2.21357                    | 0.36734                    |
| $H_{\text{atom}}(C_{\text{atom}} - Br_{\text{atom}})$ , $m = 1, 2, 3$<br>(C-Br (iv))    | Br   | -0.18114                | 0                       | 0                       | 0                       | -151.79683                                        | 1.15169                                 | 0.90664                                 | -15.00689                           | -14.81063                   | 66.10            | 113.90            | 28.76             | 2.21357                    | 0.36734                    |
| $H_{\text{atom}}(C_{\text{atom}} - Br_{\text{atom}})$ , $m = 1, 2, 3$<br>(C-Br (v))     | C    | -0.46459                | -0.92918                | 0                       | 0                       | -153.09546                                        | 0.91771                                 | 0.83885                                 | -16.21952                           | -16.02866                   | 62.67            | 117.33            | 26.55             | 2.21237                    | 0.36518                    |
| $H_{\text{atom}}(C_{\text{atom}} - Br_{\text{atom}})$ , $m = 1, 2, 3$<br>(C-Br (vi))    | Br   | -0.46459                | -0.92918                | 0                       | 0                       | -153.09546                                        | 1.15169                                 | 0.83885                                 | -16.21952                           | -16.02866                   | 62.67            | 117.33            | 26.55             | 2.21237                    | 0.36518                    |
| $H_{\text{atom}}(C_{\text{atom}} - Br_{\text{atom}})$ , $m = 1, 2, 3$<br>(C-Br (vii))   | C    | -0.92918                | 0                       | 0                       | 0                       | -152.44487                                        | 0.91771                                 | 0.86359                                 | -15.75493                           | -15.56407                   | 77.49            | 102.51            | 41.48             | 1.23564                    | 0.18708                    |
| $H_{\text{atom}}(C_{\text{atom}} - Br_{\text{atom}})$ , $m = 1, 2, 3$<br>(C-Br (viii))  | Br   | -0.92918                | 0                       | 0                       | 0                       | -152.44487                                        | 1.15169                                 | 0.86359                                 | -15.75493                           | -15.56407                   | 77.49            | 102.51            | 41.48             | 1.23564                    | 0.18708                    |
| $H_{\text{atom}}(C_{\text{atom}} - Br_{\text{atom}})$ , $m = 1, 2, 3$<br>(C-Br (ix))    | C    | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                        | 0.91771                                 | 0.81549                                 | -16.68412                           | -16.49325                   | 68.47            | 111.53            | 35.84             | 1.35486                    | 0.29953                    |
| $H_{\text{atom}}(C_{\text{atom}} - Br_{\text{atom}})$ , $m = 1, 2, 3$<br>(C-Br (x))     | Br   | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                        | 1.15169                                 | 0.81549                                 | -16.68412                           | -16.49325                   | 68.47            | 111.53            | 35.84             | 1.35486                    | 0.29953                    |
| $H_{\text{atom}}(C_{\text{atom}} - Br_{\text{atom}})$ , $m = 1, 2, 3$<br>(C-Br (xi))    | C    | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                        | 0.91771                                 | 0.77247                                 | -17.61350                           | -17.42244                   | 61.10            | 118.90            | 31.37             | 1.42988                    | 0.37326                    |
| $H_{\text{atom}}(C_{\text{atom}} - Br_{\text{atom}})$ , $m = 1, 2, 3$<br>(C-Br (xii))   | Br   | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                        | 1.15169                                 | 0.77247                                 | -17.61350                           | -17.42244                   | 61.10            | 118.90            | 31.37             | 1.42988                    | 0.37326                    |
| $H_{\text{atom}}(C_{\text{atom}} - Br_{\text{atom}})$ , $m = 1, 2, 3$<br>(C-Br (xiii))  | C    | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                        | 0.91771                                 | 0.86359                                 | -15.75493                           | -15.56407                   | 63.82            | 116.18            | 30.08             | 1.83879                    | 0.38106                    |
| $H_{\text{atom}}(C_{\text{atom}} - Br_{\text{atom}})$ , $m = 1, 2, 3$<br>(C-Br (xiv))   | Br   | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                        | 1.15169                                 | 0.86359                                 | -15.75493                           | -15.56407                   | 63.82            | 116.18            | 30.08             | 1.83879                    | 0.38106                    |
| $H_{\text{atom}}(C_{\text{atom}} - Br_{\text{atom}})$ , $m = 1, 2, 3$<br>(C-Br (xv))    | C    | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                        | 0.91771                                 | 0.81549                                 | -16.68412                           | -16.49325                   | 56.41            | 123.59            | 26.06             | 1.90890                    | 0.45117                    |
| $H_{\text{atom}}(C_{\text{atom}} - Br_{\text{atom}})$ , $m = 1, 2, 3$<br>(C-Br (xvi))   | Br   | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                        | 1.15169                                 | 0.81549                                 | -16.68412                           | -16.49325                   | 56.41            | 123.59            | 26.06             | 1.90890                    | 0.45117                    |
| $H_{\text{atom}}(C_{\text{atom}} - Br_{\text{atom}})$ , $m = 1, 2, 3$<br>(C-Br (xvii))  | C    | -0.92918                | -0.92918                | -0.92918                | -0.72457                | -154.71860                                        | 0.91771                                 | 0.75889                                 | -17.92866                           | -17.73779                   | 48.21            | 131.79            | 21.74             | 1.93754                    | 0.50570                    |
| $H_{\text{atom}}(C_{\text{atom}} - Br_{\text{atom}})$ , $m = 1, 2, 3$<br>(C-Br (xviii)) | Br   | -0.92918                | -0.92918                | -0.92918                | -0.72457                | -154.71860                                        | 1.15169                                 | 0.75889                                 | -17.92866                           | -17.73779                   | 48.21            | 131.79            | 21.74             | 1.93754                    | 0.50570                    |
| $H_{\text{atom}}(C_{\text{atom}} - Br_{\text{atom}})$ , $m = 1, 2, 3$<br>(C-Br (xix))   | C    | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                        | 0.91771                                 | 0.77247                                 | -17.61350                           | -17.42244                   | 48.50            | 131.70            | 21.90             | 1.97162                    | 0.51388                    |
| $H_{\text{atom}}(C_{\text{atom}} - Br_{\text{atom}})$ , $m = 1, 2, 3$<br>(C-Br (xx))    | Br   | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                        | 1.15169                                 | 0.77247                                 | -17.61350                           | -17.42244                   | 48.50            | 131.70            | 21.90             | 1.97162                    | 0.51388                    |
| $H_{\text{atom}}(C_{\text{atom}} - Br_{\text{atom}})$ , $m = 1, 2, 3$<br>(C-Br (xxi))   | C    | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.41399                                        | 0.91771                                 | 0.76765                                 | -17.92866                           | -17.73779                   | 50.04            | 129.96            | 22.66             | 1.94462                    | 0.49298                    |
| $H_{\text{atom}}(C_{\text{atom}} - Br_{\text{atom}})$ , $m = 1, 2, 3$<br>(C-Br (xxii))  | Br   | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.41399                                        | 1.15169                                 | 0.76765                                 | -17.92866                           | -17.73779                   | 50.04            | 129.96            | 22.66             | 1.94462                    | 0.49298                    |
| $H_{\text{atom}}(C_{\text{atom}} - Br_{\text{atom}})$ , $m = 1, 2, 3$<br>(C-Br (xxiii)) | C    | -0.72457                | -0.92918                | -0.92918                | 0                       | -154.9863                                         | 0.91771                                 | 0.78155                                 | -17.40869                           | -17.21783                   | 52.78            | 127.22            | 24.04             | 1.92443                    | 0.47279                    |
| $H_{\text{atom}}(C_{\text{atom}} - Br_{\text{atom}})$ , $m = 1, 2, 3$<br>(C-Br (xxiv))  | Br   | -0.72457                | -0.92918                | -0.92918                | 0                       | -154.9863                                         | 1.15169                                 | 0.78155                                 | -17.40869                           | -17.21783                   | 52.78            | 127.22            | 24.04             | 1.92443                    | 0.47279                    |
| $H_{\text{atom}}(C_{\text{atom}} - Br_{\text{atom}})$ , $m = 1, 2, 3$<br>(C-Br (xxv))   | C    | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.41399                                        | 0.91771                                 | 0.76765                                 | -17.92866                           | -17.73779                   | 50.04            | 129.96            | 22.66             | 1.94462                    | 0.49298                    |
| $H_{\text{atom}}(C_{\text{atom}} - Br_{\text{atom}})$ , $m = 1, 2, 3$<br>(C-Br (xxvi))  | Br   | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.41399                                        | 1.15169                                 | 0.76765                                 | -17.92866                           | -17.73779                   | 50.04            | 129.96            | 22.66             | 1.94462                    | 0.49298                    |

Table 15.42. The energy parameters (eV) of functional groups of branched-chain alkyl bromides.

Table 13.42. The energy parameters (eV) of functional groups of branched-then allyl boundaries.

| Parameters | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ | $C-Br$ |  |
|------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--|
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Table 15.43. The total bond energies of branched-chain alkyl bromides calculated using the functional group composition and the energies of Table 15.42 compared to the experimental values [2]. The magnetic energy  $E_{ms}$  that is subtracted from the weighted sum of the  $E_{\theta}^{(atom)}$  ( $eV$ ) values based on composition is given by (15.53).

| Formula                            | Name                       | C-Br (i) | C-Br (ii) | C-Br (iii) | CH <sub>3</sub> | CH <sub>2</sub> | CH (i) | CH (ii) | C-C (a) | C-C (b) | C-C (c) | C-C (d) | C-C (e) | C-C (f) | $E_{ms}$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|------------------------------------|----------------------------|----------|-----------|------------|-----------------|-----------------|--------|---------|---------|---------|---------|---------|---------|---------|----------|-----------------------------------|-------------------------------------|----------------|
| CH <sub>3</sub> Br                 | Tribromomethane            | 0        | 4         | 0          | 0               | 0               | 0      | 0       | 0       | 0       | 0       | 0       | 0       | 0       | -1       | 11.25929                          | 11.196                              | -0.00566       |
| CH <sub>2</sub> Br <sub>2</sub>    | Dibromomethane             | 3        | 0         | 0          | 0               | 0               | 0      | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 0        | 12.87698                          | 12.919                              | 0.00323        |
| CHBr <sub>3</sub>                  | Bromomethane               | 1        | 0         | 0          | 1               | 0               | 0      | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 0        | 15.67551                          | 15.732                              | 0.00360        |
| C <sub>2</sub> H <sub>5</sub> Br   | 1-Bromopropane             | 0        | 1         | 1          | 0               | 0               | 0      | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 0        | 28.03959                          | 27.953                              | -0.00308       |
| C <sub>3</sub> H <sub>7</sub> Br   | 2-Bromopropane             | 0        | 0         | 1          | 1               | 2               | 0      | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 0        | 40.19709                          | 40.160                              | -0.00093       |
| C <sub>4</sub> H <sub>9</sub> Br   | 2,3-Dibromo-2-methylbutane | 1        | 0         | 0          | 3               | 0               | 1      | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 0        | 40.29798                          | 40.288                              | -0.00024       |
| C <sub>5</sub> H <sub>11</sub> Br  | 1-Bromohexane              | 0        | 0         | 1          | 1               | 5               | 0      | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 0        | 68.48143                          | 68.477                              | -0.00007       |
| C <sub>6</sub> H <sub>13</sub> Br  | 1-Bromohexane              | 0        | 0         | 1          | 1               | 6               | 0      | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 0        | 76.67019                          | 76.634                              | -0.00047       |
| C <sub>7</sub> H <sub>15</sub> Br  | 1-Bromooctane              | 0        | 0         | 1          | 1               | 7               | 0      | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 0        | 88.82789                          | 88.783                              | -0.00051       |
| C <sub>8</sub> H <sub>17</sub> Br  | 1-Bromodecane              | 0        | 0         | 1          | 1               | 11              | 0      | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 0        | 100.96359                         | 100.952                             | -0.00033       |
| C <sub>9</sub> H <sub>19</sub> Br  | 1-Bromododecane            | 0        | 0         | 1          | 1               | 15              | 0      | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 0        | 149.61639                         | 149.573                             | -0.00029       |
| C <sub>10</sub> H <sub>21</sub> Br | 1-Bromotetradecane         | 0        | 0         | 1          | 1               | 19              | 0      | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 0        | 198.24719                         | 198.192                             | -0.00028       |

Table 15.44. The bond angle parameters of branched-chain alkyl bromides and experimental values [1]. In the calculation of  $\theta_i$ , the parameters from the preceding angle were used.  $E_i$  is  $E_i^{(atom - atom, msp, AO)}$ .

| Atom of Angle                             | $2\phi_1$<br>(Bond 1<br>( $\phi_1$ )) | $2\phi_2$<br>(Bond 2<br>( $\phi_2$ )) | $2\phi_3$<br>(Bond 3<br>( $\phi_3$ )) | $E_i^{(atom)}$<br>Atom 1<br>Hybridization<br>Designation<br>(Table 15.3.A) | $E_i^{(atom)}$<br>Atom 2<br>Hybridization<br>Designation<br>(Table 15.3.A) | $C_1$   | $C_2$   | $C_3$                     | $C_4$ | $\phi_i$<br>( $^\circ$ ) | $E_i$<br>(eV) | $\phi_i$<br>( $^\circ$ ) | $\theta_i$<br>( $^\circ$ ) | Cal.<br>$\theta_i$<br>( $^\circ$ ) | Exp. $\theta$<br>( $^\circ$ )                                                  |
|-------------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|----------------------------------------------------------------------------|----------------------------------------------------------------------------|---------|---------|---------------------------|-------|--------------------------|---------------|--------------------------|----------------------------|------------------------------------|--------------------------------------------------------------------------------|
| $\angle BrC_1C_2$<br>( $C_1 - Br$ (i))    | 3.66790                               | 3.66790                               | 6.0836                                | -15.18824<br>$Br$                                                          | 2                                                                          | 0.95982 | 0.95982 | 0.74081<br>(Eq. (15.112)) | 1     |                          | -0.92918      |                          |                            | 112.00                             | 112.2<br>(methyl bromide)<br>113.2<br>(dibromomethane)<br>111.7<br>(bromoform) |
| $\angle H^iC_1C_2$<br>( $C_1 - Br$ (iii)) | 2.1106                                | 3.66790                               | 4.8312                                | -15.53033<br>$C_s$                                                         | 5                                                                          | 0.87495 | 0.91771 | 0.80929<br>(Eq. (15.63))  | 0.75  | 1.04887                  | 0             |                          |                            | 110.33                             | 109<br>(dibromomethane)                                                        |
| $\angle H^iC_1C_2$<br>( $C_1 - Br$ (iii)) | 2.09711                               | 2.10711                               | 3.4252                                | -15.75493<br>$C_s$                                                         | 7                                                                          | 0.86339 | 1       | 1                         | 0.75  | 1.15796                  | 0             |                          |                            | 109.50                             |                                                                                |
| $\angle C_1C_2C_3$<br>( $C_1 - Br$ (iii)) | 2.91347                               | 3.65437                               | 5.4247                                | -15.75493<br>$C_s$                                                         | 7                                                                          | 0.86339 | 0.86339 | 0.74081<br>(Eq. (15.112)) | 1     |                          | -0.72457      |                          |                            | 110.44                             | 110<br>(1,3-dibromomethane)<br>109.0<br>(1,1,1-trifluoroethane)                |
| $\angle H^iC_1C_2$<br>( $C_1 - Br$ (iii)) | 2.1106                                | 2.1106                                | 3.4252                                | -15.75493<br>$C_s$                                                         | 7                                                                          | 0.86339 | 1       | 1                         | 0.75  | 1.15796                  | 0             |                          |                            | 108.44                             | 107<br>(propane)                                                               |
| $\angle C_1C_2C_3$<br>( $C_1 - Br$ (iii)) |                                       |                                       |                                       |                                                                            |                                                                            |         |         |                           |       |                          |               |                          |                            |                                    | 112<br>(propane)<br>113.8<br>(butane)<br>110.8<br>(isobutane)                  |
| $\angle C_1C_2C_3$<br>( $C_1 - Br$ (iii)) |                                       |                                       |                                       |                                                                            |                                                                            |         |         |                           |       |                          |               |                          |                            |                                    | 111.0<br>(nitroethane)<br>111.4<br>(isobutane)                                 |
| $\angle C_1C_2C_3$<br>( $C_1 - Br$ (iii)) | 2.09711                               | 2.09711                               | 3.4252                                | -15.75493<br>$C_s$                                                         | 7                                                                          | 0.86339 | 1       | 1                         | 0.75  | 1.15796                  | 0             |                          |                            | 109.30                             |                                                                                |
| $\angle C_1C_2C_3$<br>( $C_1 - Br$ (iii)) |                                       |                                       |                                       |                                                                            |                                                                            |         |         |                           |       |                          |               |                          |                            | 109.44                             |                                                                                |
| $\angle C_1C_2C_3$<br>( $C_1 - Br$ (iii)) |                                       |                                       |                                       |                                                                            |                                                                            |         |         |                           |       |                          |               |                          |                            | 109.44                             |                                                                                |
| $\angle C_1C_2C_3$<br>( $C_1 - Br$ (iii)) | 2.91347                               | 2.91347                               | 4.7958                                | -16.68412<br>$C_s$                                                         | 25                                                                         | 0.81549 | 0.81549 | 1                         | 1     | 0.81549                  | -1.85836      |                          |                            | 110.67                             | 110.8<br>(isobutane)                                                           |
| $\angle C_1C_2C_3$<br>( $C_1 - Br$ (iii)) | 2.91347                               | 2.11325                               | 4.1633                                | -15.53033<br>$C_s$                                                         | 5                                                                          | 0.87495 | 0.91771 | 0.75                      | 1     | 1.04887                  | 0             |                          |                            | 110.76                             |                                                                                |
| $\angle C_1C_2C_3$<br>( $C_1 - Br$ (iii)) | 2.91347                               | 2.09711                               | 4.1633                                | -15.53033<br>$C_s$                                                         | 5                                                                          | 0.87495 | 0.91771 | 0.75                      | 1     | 1.04887                  | 0             |                          |                            | 111.27                             | 111.4<br>(isobutane)                                                           |
| $\angle C_1C_2C_3$<br>( $C_1 - Br$ (iii)) | 2.90227                               | 2.90227                               | 4.7958                                | -15.53033<br>$C_s$                                                         | 5                                                                          | 0.87495 | 0.91771 | 0.75                      | 1     | 1.04887                  | -1.85836      |                          |                            | 111.27                             | 111.4<br>(isobutane)                                                           |
| $\angle C_1C_2C_3$<br>( $C_1 - Br$ (iii)) |                                       |                                       |                                       |                                                                            |                                                                            |         |         |                           |       |                          |               |                          |                            | 109.50                             |                                                                                |

# ALKYL IODIDES ( $C_n H_{2n+2-m} I_m$ , $n=1,2,3,4,5\ldots\infty$ $m=1,2,3\ldots\infty$ )

The branched-chain alkyl iodides,  $C_n H_{2n+2-m} I_m$ , may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds wherein at least one  $H$  is replaced by an iodine atom. The  $C-I$  bond comprises a functional group for  $I$  replacing a  $H$  of methane ( $CH_3I$ ) or for  $I$  replacing a  $H$  of an alkane corresponding to the series  $C_n H_{2n+2-m} I_m$ . The  $C-I$  bond of each of  $CH_2I_2$  and  $CHI_3$  comprise separate functional groups due to the limitation of the minimum energy of  $I$  matched to that of the  $C2sp^3$  HO. The methyl, methylene, methylene functional groups are equivalent to those of branched-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the  $C-I$  functional groups comprises the hybridization of the  $2s$  and  $2p$  AOs of each  $C$  to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the  $I$  AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl iodides, the energy of iodine is less than the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). Thus,  $c_2$  in Eq. (15.52) is one, and the energy matching condition is determined by the  $C_2$  parameter. Then, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)). The  $I$  AO has an energy of  $E(I) = -10.45126 \text{ eV}$ . To meet the equipotential condition of the union of the  $C-I$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $C_2$  of Eq. (15.51) for the  $C-I$ -bond MO given by Eqs. (15.68) and (15.70) is

$$C_2(C2sp^3HO \text{ to } I) = \frac{E(I)}{E(C, 2sp^3)} c_2(C2sp^3HO) = \frac{-10.45126 \text{ eV}}{-14.63489 \text{ eV}} (0.91771) = 0.65537 \quad (15.113)$$

The valence energy of the carbon  $2p$  is  $-11.2603 \text{ eV}$  and that of the  $I$  AO is  $-10.45126 \text{ eV}$ .

The energy difference is positive. Thus, based on the maximum charge density on the  $C2sp^3$

HO  $E_T(\text{atom} - \text{atom}, \text{msp}^3, \text{AO})$  of the  $C - I$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $I$  atoms to the MO is  $-0.36229 \text{ eV}$  (Eqs. (15.18-15.20 and Eq. (15.29) with a linear combination of  $s=1$ ,  $E_T(\text{atom} - \text{atom}, \text{msp}^3, \text{AO}) = -0.72457 \text{ eV}$  and  $E_T(\text{atom} - \text{atom}, \text{msp}^3, \text{AO}) = 0$ ) for methyl and alkyl iodides,  $-0.18114 \text{ eV}$  for diiodomethane, 5 and 0 for  $\text{CHI}_3$ .

The symbols of the functional groups of branched-chain alkyl iodides are given in Table 15.45. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl iodides are given in Tables 15.46, 15.47, and 15.48, respectively. The total energy of each branched-chain 10 alkyl iodide given in Table 15.49 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.48 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{\text{mag}}$  that was subtracted from the weighted sum of the  $E_D(\text{Group})$  ( $\text{eV}$ ) values based on composition is given by Eq. (15.58). The  $C - C$  bonds to the  $\text{CHI}$  group (one  $H$  bond to  $C$ ) were each 15 treated as an iso  $C - C$  bond. The  $C - C$  bonds to the  $\text{CI}$  group (no  $H$  bonds to  $C$ ) were each treated as a tert-butyl  $C - C$ .  $E_{\text{mag}}$  is subtracted for each t-butyl group. The bond angle parameters of branched-chain alkyl iodides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.113) are given in Table 15.50.

20 Table 15.45. The symbols of functional groups of branched-chain alkyl iodides.

| Functional Group                                                        | Group Symbol              |
|-------------------------------------------------------------------------|---------------------------|
| CI of $\text{CH}_3\text{I}$ and $\text{C}_n\text{H}_{2n+2-m}\text{I}_m$ | $C - I$ (i)               |
| CI of $\text{CH}_2\text{I}_2$                                           | $C - I$ (ii)              |
| CI of $\text{CHI}_3$                                                    | $C - I$ (iii)             |
| $\text{CH}_3$ group                                                     | $C - H$ ( $\text{CH}_3$ ) |
| $\text{CH}_2$ group                                                     | $C - H$ ( $\text{CH}_2$ ) |
| CH                                                                      | $C - H$                   |
| CC bond (n-C)                                                           | $C - C$ (a)               |
| CC bond (iso-C)                                                         | $C - C$ (b)               |
| CC bond (tert-C)                                                        | $C - C$ (c)               |
| CC (iso to iso-C)                                                       | $C - C$ (d)               |
| CC (t to t-C)                                                           | $C - C$ (e)               |
| CC (t to iso-C)                                                         | $C - C$ (f)               |



Table 15.46. The geometrical bond parameters of branched-chain alkyl iodides and experimental values [1].

| Parameter               | C-I (i)<br>Group         | C-I (ii)<br>Group        | C-I (iii)<br>Group             | C-H (CH <sub>3</sub> )<br>Group                 | C-H (CH <sub>2</sub> )<br>Group                 | C-H (CH)<br>Group    | C-C (a)<br>Group                        | C-C (b)<br>Group                        | C-C (c)<br>Group                        | C-C (d)<br>Group                        | C-C (e)<br>Group                        | C-C (f)<br>Group                        |
|-------------------------|--------------------------|--------------------------|--------------------------------|-------------------------------------------------|-------------------------------------------------|----------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|
| $\sigma$ (Å)            | 2.67103                  | 2.68865                  | 2.70662                        | 1.64920                                         | 1.67122                                         | 1.67465              | 2.12499                                 | 2.12499                                 | 2.10725                                 | 2.12499                                 | 2.10725                                 | 2.10725                                 |
| $c'$ (Å)                | 2.01881                  | 2.02546                  | 2.03222                        | 1.04856                                         | 1.05553                                         | 1.05661              | 1.45744                                 | 1.45744                                 | 1.45164                                 | 1.45744                                 | 1.45164                                 | 1.45164                                 |
| Bond Length<br>2c' (Å)  | 2.13662                  | 2.14365                  | 2.15081                        | 1.10974                                         | 1.11713                                         | 1.11827              | 1.54280                                 | 1.54280                                 | 1.53635                                 | 1.54280                                 | 1.53635                                 | 1.53635                                 |
| Exp. Bond Length<br>(Å) | 2.132<br>(methyl iodide) | 2.132<br>(methyl iodide) | 2.15<br>(carbon tetrachloride) | 1.107<br>(C-H propane)<br>1.117<br>(C-H butane) | 1.107<br>(C-H propane)<br>1.117<br>(C-H butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $h, c$ (Å)              | 1.74894                  | 1.76815                  | 1.78770                        | 1.27295                                         | 1.29569                                         | 1.29924              | 1.54616                                 | 1.54616                                 | 1.52750                                 | 1.54616                                 | 1.52750                                 | 1.52750                                 |
| $e$                     | 0.75582                  | 0.75334                  | 0.75083                        | 0.63380                                         | 0.63159                                         | 0.63095              | 0.68600                                 | 0.68600                                 | 0.68888                                 | 0.68600                                 | 0.68888                                 | 0.68888                                 |

Table 15.47. The MO to HO intercept geometrical bond parameters of branched-chain alkyl iodides.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{msp}^3, \Delta O)$ .

| Bond                                           | Atom  | $E_T$<br>(eV)<br>Bond 1 | $E_T$<br>(eV)<br>Bond 2 | $E_T$<br>(eV)<br>Bond 3 | $E_T$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>$C2sp^3$<br>(eV) | $r_{\text{final}}$<br>( $a_0$ ) | $r_{\text{final}}$<br>( $a_0$ ) | $E_{\text{rotat}}$<br>(eV)<br>Final | $E(C2sp^3)$<br>(eV)<br>Final | $\theta'$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | $d_1$<br>( $a_0$ ) | $d_2$<br>( $a_0$ ) |
|------------------------------------------------|-------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------------------------|---------------------------------|---------------------------------|-------------------------------------|------------------------------|---------------------------|----------------------------|----------------------------|--------------------|--------------------|
| $C^*H_3I$<br>( $C_0-I$ (i))                    | $C^*$ | -0.18114                | 0                       | 0                       | 0                       | -151.79683                                | 0.91771                         | 0.90664                         | -15.00689                           | -14.81603                    | 69.63                     | 110.37                     | 29.08                      | 2.33442            | 0.31560            |
| $C^*H_3I$<br>( $C_0-I$ (ii))                   | $I$   | -0.18114                | 0                       | 0                       | 0                       |                                           | 1.30183                         | 0.90664                         | -15.00689                           |                              | 69.63                     | 110.37                     | 29.08                      | 2.33442            | 0.31560            |
| $-H_3C^*C^*I$<br>( $C_0-I$ (i))                | $C^*$ | -0.18114                | -0.92918                | 0                       | 0                       | -152.72602                                | 0.91771                         | 0.83377                         | -15.93608                           | -15.74521                    | 63.16                     | 116.84                     | 25.82                      | 2.40456            | 0.38554            |
| $-H_3C^*C^*I$<br>( $C_0-I$ (ii))               | $I$   | -0.18114                | 0                       | 0                       | 0                       |                                           | 1.30183                         | 0.90664                         | -15.00689                           |                              | 69.63                     | 110.37                     | 29.08                      | 2.33442            | 0.31560            |
| $C^*H_3I_2$<br>( $C_0-I$ (iii))                | $C^*$ | -0.09057                | 0                       | 0                       | 0                       | -151.70626                                | 0.91771                         | 0.91214                         | -14.91632                           | -14.72546                    | 68.61                     | 111.39                     | 28.71                      | 2.35818            | 0.33272            |
| $C^*H_3I_2$<br>( $C_0-I$ (iv))                 | $I$   | -0.09057                | 0                       | 0                       | 0                       |                                           | 1.30183                         | 0.91214                         | -14.91632                           |                              | 68.61                     | 111.39                     | 28.71                      | 2.35818            | 0.33272            |
| $C_0H_3I_3$<br>( $C_0-I$ (v))                  | $C_0$ | 0                       | 0                       | 0                       | 0                       | -151.61569                                | 0.91771                         | 0.91771                         | -14.82575                           | -14.63489                    | 67.56                     | 112.44                     | 28.32                      | 2.38256            | 0.35055            |
| $C_0H_3I_3$<br>( $C_0-I$ (vi))                 | $I$   | 0                       | 0                       | 0                       | 0                       |                                           | 1.30183                         | 0.91771                         | -14.82575                           | -14.63489                    | 67.56                     | 112.44                     | 28.32                      | 2.38256            | 0.35055            |
| $C^*H_3(C^*H_3)$<br>( $C_0-H$ (i))             | $C^*$ | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                | 0.91771                         | 0.86359                         | -15.75493                           | -15.56407                    | 71.49                     | 100.51                     | 41.48                      | 1.23564            | 0.18708            |
| $C^*H_3(C^*H_3)$<br>( $C_0-H$ (ii))            | $C^*$ | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                | 0.91771                         | 0.81549                         | -16.68412                           | -16.49325                    | 68.47                     | 111.53                     | 35.84                      | 1.35486            | 0.29953            |
| $C^*H_3(C^*H_3)$<br>( $C_0-H$ (iii))           | $C^*$ | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                | 0.91771                         | 0.7247                          | -17.61330                           | -17.42244                    | 61.10                     | 118.90                     | 31.37                      | 1.42988            | 0.37356            |
| $H_3C^*C^*H_3C^*H_3$<br>( $C-C$ (a))           | $C^*$ | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                | 0.91771                         | 0.86359                         | -15.75493                           | -15.56407                    | 63.82                     | 116.18                     | 30.08                      | 1.83879            | 0.38106            |
| $H_3C^*C^*H_3C^*H_3$<br>( $C-C$ (b))           | $C^*$ | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                | 0.91771                         | 0.81549                         | -16.68412                           | -16.49325                    | 56.41                     | 125.59                     | 26.06                      | 1.90890            | 0.45117            |
| $R-H_3C^*C^*(H_3C^*-R)HC^*H_3$<br>( $C-C$ (c)) | $C^*$ | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                | 0.91771                         | 0.7247                          | -17.61330                           | -17.42244                    | 48.30                     | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| $R-H_3C^*C^*(H_3C^*-R)HC^*H_3$<br>( $C-C$ (d)) | $C^*$ | -0.92918                | -0.92918                | -0.92918                | -0.72457                | -154.71860                                | 0.91771                         | 0.75889                         | -17.92866                           | -17.73779                    | 48.21                     | 131.79                     | 21.74                      | 1.95734            | 0.50570            |
| $twcC^*C^*(H_3C^*-R)HC^*H_3$<br>( $C-C$ (e))   | $C^*$ | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                | 0.91771                         | 0.77347                         | -17.61330                           | -17.42244                    | 48.30                     | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| $twcC^*C^*(H_3C^*-R)HC^*H_3$<br>( $C-C$ (f))   | $C^*$ | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.51999                                | 0.91771                         | 0.76765                         | -17.92866                           | -17.73779                    | 50.04                     | 129.96                     | 22.66                      | 1.94462            | 0.49298            |
| $twcC^*C^*(H_3C^*-R)HC^*H_3$<br>( $C-C$ (g))   | $C^*$ | -0.72457                | -0.92918                | -0.92918                | 0                       | -154.19863                                | 0.91771                         | 0.78155                         | -17.40869                           | -17.21783                    | 52.78                     | 127.22                     | 24.04                      | 1.92443            | 0.47279            |
| $twcC^*C^*(H_3C^*-R)HC^*H_3$<br>( $C-C$ (h))   | $C^*$ | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.51999                                | 0.91771                         | 0.76765                         | -17.92866                           | -17.73779                    | 50.04                     | 129.96                     | 22.66                      | 1.94462            | 0.49298            |

Table 15.48. The energy parameters (eV) of functional groups of branched-chain alkyl iodides.

| Parameters                        | C-I<br>(i) | C-I<br>(ii) | C-I<br>(iii) | CH <sub>3</sub><br>Group | CH <sub>2</sub><br>Group | C-H<br>Group | C-C (a)<br>Group | C-C (b)<br>Group | C-C (c)<br>Group | C-C (d)<br>Group | C-C (e)<br>Group | C-C (f)<br>Group | C-C (f)<br>Group |
|-----------------------------------|------------|-------------|--------------|--------------------------|--------------------------|--------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| $\eta_1$                          | 1          | 1           | 1            | 3                        | 2                        | 1            | 1                | 1                | 1                | 1                | 1                | 1                | 1                |
| $\eta_2$                          | 0          | 0           | 0            | 2                        | 1                        | 0            | 0                | 0                | 0                | 0                | 0                | 0                | 0                |
| $\eta_3$                          | 0          | 0           | 0            | 0                        | 0                        | 0            | 0                | 0                | 0                | 0                | 0                | 0                | 0                |
| $C_1$                             | 0.5        | 0.5         | 0.5          | 0.75                     | 0.75                     | 0.75         | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              |
| $C_2$                             | 0.65537    | 0.65537     | 0.65537      | 1                        | 1                        | 1            | 1                | 1                | 1                | 1                | 1                | 1                | 1                |
| $C_3$                             | 1          | 1           | 1            | 1                        | 1                        | 1            | 1                | 1                | 1                | 1                | 1                | 1                | 1                |
| $C_4$                             | 1          | 1           | 1            | 0.91771                  | 0.91771                  | 0.91771      | 0.91771          | 0.91771          | 0.91771          | 0.91771          | 0.91771          | 0.91771          | 0.91771          |
| $C_5$                             | 1          | 0           | 1            | 0                        | 1                        | 1            | 0                | 0                | 0                | 1                | 1                | 0                | 0                |
| $C_6$                             | 2          | 2           | 2            | 1                        | 1                        | 1            | 2                | 2                | 2                | 2                | 2                | 2                | 2                |
| $C_7$                             | 0          | 0           | 0            | 3                        | 2                        | 1            | 0                | 0                | 0                | 0                | 0                | 0                | 0                |
| $C_{10}$                          | 0.5        | 0.5         | 0.5          | 0.75                     | 0.75                     | 0.75         | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              |
| $C_{11}$                          | 0.65537    | 0.65537     | 0.65537      | 1                        | 1                        | 1            | 1                | 1                | 1                | 1                | 1                | 1                | 1                |
| $C_{12}$                          | -26.59109  | -26.34902   | -26.10696    | -107.32728               | -70.41425                | -35.12015    | -28.79214        | -28.79214        | -29.10112        | -28.79214        | -29.10112        | -29.10112        | -29.10112        |
| $V_e$ (eV)                        | 6.75951    | 6.71739     | 6.69505      | 38.92728                 | 25.78002                 | 12.87680     | 9.3352           | 9.3352           | 9.37273          | 9.3352           | 9.37273          | 9.37273          | 9.37273          |
| $T$ (eV)                          | 4.97768    | 4.82280     | 4.82280      | 32.53914                 | 21.06675                 | 10.48582     | 6.77464          | 6.77464          | 6.90500          | 6.77464          | 6.90500          | 6.90500          | 6.90500          |
| $V_{\text{ion}}$ (eV)             | -2.48884   | -2.45002    | -2.41140     | -16.20957                | -10.53357                | -5.24291     | -3.38732         | -3.38732         | -3.45250         | -3.38732         | -3.45250         | -3.45250         | -3.45250         |
| $E_{\text{ion}}$ (eV)             | -14.63489  | -14.63489   | -14.63489    | -15.56407                | -15.56407                | -14.63489    | -15.56407        | -15.56407        | -15.56407        | -15.56407        | -15.56407        | -15.56407        | -15.56407        |
| $\Delta E_{\text{ion}}$ (eV)      | -0.36229   | -0.18114    | 0            | 0                        | 0                        | 0            | 0                | 0                | 0                | 0                | 0                | 0                | 0                |
| $E_{\text{ion}}$ (eV)             | -14.29907  | -14.45375   | -14.63489    | -15.56407                | -15.56407                | -14.63489    | -15.56407        | -15.56407        | -15.56407        | -15.56407        | -15.56407        | -15.56407        | -15.56407        |
| $E_{\text{ion}}$ (eV)             | -31.63554  | -31.63555   | -31.63554    | -67.69451                | -49.66493                | -31.63533    | -31.63537        | -31.63537        | -31.63533        | -31.63537        | -31.63533        | -31.63533        | -31.63533        |
| $E_{\text{ion}}$ (eV)             | -0.36229   | -0.18114    | 0            | 0                        | 0                        | 0            | -1.85836         | -1.85836         | -1.44915         | -1.85836         | -1.44915         | -1.44915         | -1.44915         |
| $E_{\text{ion}}$ (eV)             | -31.99766  | -31.81651   | -31.63537    | -67.69450                | -49.66493                | -31.63537    | -33.49373        | -33.49373        | -33.08452        | -33.49373        | -33.08452        | -33.08452        | -33.08452        |
| $\omega$ (10 <sup>11</sup> rad/s) | 10.2318    | 5.36799     | 9.90080      | 24.9286                  | 24.2751                  | 24.1759      | 9.45699          | 9.45699          | 15.4846          | 9.45699          | 15.4846          | 9.55643          | 9.55643          |
| $E_{\text{ion}}$ (eV)             | 6.73472    | 3.53331     | 6.51688      | 16.40846                 | 15.97831                 | 15.91299     | 6.21159          | 6.21159          | 10.19220         | 6.21159          | 10.19220         | 6.29021          | 6.29021          |
| $E_{\text{ion}}$ (eV)             | -0.16428   | -0.11832    | -0.15977     | -0.25352                 | -0.25017                 | -0.24966     | -0.16515         | -0.16515         | -0.20896         | -0.16515         | -0.20896         | -0.16416         | -0.16416         |
| $E_{\text{ion}}$ (eV)             | 0.06608    | 0.06608     | 0.06608      | 0.35532                  | 0.35532                  | 0.35532      | 0.12312          | 0.12312          | 0.09944          | 0.12312          | 0.09944          | 0.12312          | 0.12312          |
| $E_{\text{ion}}$ (eV)             | -0.13124   | -0.08527    | -0.12673     | -0.22757                 | -0.14502                 | -0.07200     | -0.10359         | -0.07526         | -0.15924         | -0.10359         | -0.15924         | -0.10260         | -0.10260         |
| $E_{\text{ion}}$ (eV)             | 0.14803    | 0.14803     | 0.14803      | 0.14803                  | 0.14803                  | 0.14803      | 0.14803          | 0.14803          | 0.14803          | 0.14803          | 0.14803          | 0.14803          | 0.14803          |
| $E_{\text{ion}}$ (eV)             | -32.12889  | -31.90179   | -31.76210    | -67.92207                | -49.80996                | -31.70737    | -33.59732        | -33.49373        | -33.24576        | -33.59732        | -33.24576        | -33.18712        | -33.18712        |
| $E_{\text{ion}}$ (eV)             | -14.63489  | -14.63489   | -14.63489    | -14.63489                | -14.63489                | -14.63489    | -14.63489        | -14.63489        | -14.63489        | -14.63489        | -14.63489        | -14.63489        | -14.63489        |
| $E_{\text{ion}}$ (eV)             | 0          | 0           | 0            | -13.59844                | -13.59844                | -13.59844    | 0                | 0                | 0                | 0                | 0                | 0                | 0                |
| $E_{\text{ion}}$ (eV)             | 2.71108    | 2.63201     | 2.34429      | 12.49186                 | 7.83016                  | 3.32601      | 4.32754          | 4.29921          | 3.97398          | 4.17951          | 3.62128          | 3.91734          | 3.91734          |

Table 15.49. The total bond energies of branched-chain alkyl iodides calculated using the functional group composition and the energies of Table 15.48 compared to the experimental values [2]. The magnetic energy  $E_{\text{mag}}$  that is subtracted from the weighted sum of the  $E_{\text{p}}(\text{group})$  (eV) val based on composition is given by (15.58).

| Name                   | Formula                           | C-I (i) | C-I (ii) | C-I (iii) | CH <sub>3</sub> | CH <sub>2</sub> | CH (i) | CH (ii) | C-C (a) | C-C (b) | C-C (c) | C-C (d) | C-C (e) | C-C (f) | $E_{\text{mag}}$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|------------------------|-----------------------------------|---------|----------|-----------|-----------------|-----------------|--------|---------|---------|---------|---------|---------|---------|---------|------------------|-----------------------------------|-------------------------------------|----------------|
| Tridimethylmethane     | CH <sub>3</sub>                   | 0       | 0        | 3         | 0               | 0               | 1      | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 0                | 10.5588                           | 10.05                               | 0.0444         |
| Dimethylmethane        | CH <sub>3</sub> CH <sub>3</sub>   | 0       | 2        | 0         | 0               | 1               | 0      | 0       | 0       | 0       | 0       | 0       | 0       | 0       | -1               | 12.94614                          | 12.921                              | -0.00095       |
| Iododimethylmethane    | CH <sub>3</sub> CH <sub>2</sub> I | 1       | 0        | 0         | 1               | 0               | 0      | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 0                | 15.70394                          | 15.163                              | -0.00263       |
| Iodoethylmethane       | C <sub>2</sub> H <sub>5</sub> I   | 1       | 0        | 0         | 1               | 1               | 0      | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 0                | 22.56064                          | 22.343                              | -0.00066       |
| 1-Iodopropane          | C <sub>3</sub> H <sub>7</sub> I   | 1       | 0        | 0         | 1               | 2               | 0      | 0       | 2       | 0       | 0       | 0       | 0       | 0       | 0                | 30.51834                          | 30.516                              | -0.00006       |
| 2-Iodopropane          | C <sub>3</sub> H <sub>7</sub> I   | 1       | 0        | 0         | 2               | 0               | 1      | 0       | 0       | 2       | 0       | 0       | 0       | 0       | 0                | 30.51903                          | 30.533                              | 0.00069        |
| 2-Iodo-2-methylpropane | C <sub>4</sub> H <sub>9</sub> I   | 1       | 0        | 0         | 3               | 0               | 0      | 0       | 0       | 0       | 0       | 0       | 0       | 0       | -1               | 51.96057                          | 51.999                              | -0.00119       |

Table 15.50. The bond angle parameters of branched-chain alkyl iodides and experimental values [1]. In the calculation of  $\theta_p$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(atom - atom, nsp^2, AO)$ .

| Atom 1 Angle                | $2c_1'$<br>( $\theta_1$ ) | $2c_2'$<br>( $\theta_2$ ) | $2c_3'$<br>( $\theta_3$ ) | $F_{\text{hybridize}}$<br>Atom 1 | Atom 1<br>Hybridization<br>Designation<br>(Table 15.3.A) | $F_{\text{hybridize}}$<br>Atom 2 | Atom 2<br>Hybridization<br>Designation<br>(Table 15.3.A) | $c_2$<br>Atom 1 | $c_2$<br>Atom 2 | $C_1$ | $C_2$                     | $c_1$ | $\zeta$ | $E_T$<br>(eV) | $\theta_p$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | Cal.<br>$\theta$<br>( $^\circ$ ) | Exp. $\theta$<br>( $^\circ$ )                                                                              |
|-----------------------------|---------------------------|---------------------------|---------------------------|----------------------------------|----------------------------------------------------------|----------------------------------|----------------------------------------------------------|-----------------|-----------------|-------|---------------------------|-------|---------|---------------|----------------------------|----------------------------|----------------------------|----------------------------------|------------------------------------------------------------------------------------------------------------|
| $\angle C_1 - I - (i)$      | 4.03092                   | 4.03092                   | 6.7205                    | -10.45126<br>$I$                 | 1                                                        | -10.45126<br>$I$                 | 1                                                        | 1               | 1               | 1     | 0.65337<br>(Eq. (15.113)) | 1     | 1       | -0.30228      |                            |                            |                            | 112.10                           |                                                                                                            |
| $\angle HC_1 - I$           | 2.11106                   | 4.03763                   | 5.2203                    | -14.82575<br>$C_1$               | 1                                                        | -10.45126<br>$I$                 | 1                                                        | 0.91771         | 0.91771         | 0.75  | 0.76815<br>(Eq. (15.63))  | 0.75  | 1.00000 | 0             |                            |                            |                            | 112.39                           |                                                                                                            |
| $\angle HC_1 - H$           | 2.09711                   | 2.09711                   | 3.4252                    | -15.75493<br>$C_1$               | 7                                                        | H                                | H                                                        | 0.86359         | 1               | 1     | 1                         | 0.75  | 1.15796 | 0             |                            |                            |                            | 109.50                           | 111.2<br>(methyl iodide)                                                                                   |
| $\angle C_1' - C_1' - H_1$  |                           |                           |                           |                                  |                                                          |                                  |                                                          |                 |                 |       |                           |       |         |               |                            | 70.56                      |                            | 109.44                           |                                                                                                            |
| $\angle C_1' - C_1' - I$    | 2.91547                   | 4.03763                   | 5.7939                    | -15.55033<br>$C_1'$              | 5                                                        | -10.45126<br>$I$                 | 1                                                        | 0.87495         | 0.87495         | 1     | 0.65337<br>(Eq. (15.113)) | 1     | 0.7495  | -0.36228      |                            |                            |                            | 111.86                           |                                                                                                            |
| $\angle HC_1' - H_1$        | 2.11106                   | 2.11106                   | 3.4252                    | -15.75493<br>$C_1'$              | 7                                                        | H                                | H                                                        | 0.86359         | 1               | 1     | 1                         | 0.75  | 1.15796 | 0             |                            |                            |                            | 108.44                           | 107<br>(propane)                                                                                           |
| $\angle C_1' - C_1' - C_1'$ |                           |                           |                           |                                  |                                                          |                                  |                                                          |                 |                 |       |                           |       |         |               |                            |                            |                            | 110.49                           | 112<br>(propane)<br>115.8<br>(butane)<br>110.8<br>(isobutane)<br>111.0<br>(butane)<br>111.4<br>(isobutane) |
| $\angle C_1' - C_1' - H_1$  | 2.09711                   | 2.09711                   | 3.4252                    | -15.75493<br>$C_1'$              | 7                                                        | H                                | H                                                        | 0.86359         | 1               | 1     | 1                         | 0.75  | 1.15796 | 0             |                            |                            |                            | 109.50                           |                                                                                                            |
| $\angle C_1' - C_1' - C_1'$ |                           |                           |                           |                                  |                                                          |                                  |                                                          |                 |                 |       |                           |       |         |               |                            | 70.56                      |                            | 109.44                           |                                                                                                            |
| $\angle C_1' - C_1' - H_1$  | 2.91547                   | 2.91547                   | 4.7938                    | -16.68412<br>$C_1'$              | 25                                                       | -16.68412<br>$C_1'$              | 25                                                       | 0.81549         | 0.81549         | 1     | 1                         | 1     | 0.81549 | -1.85836      |                            |                            |                            | 110.67                           | 110.8<br>(isobutane)                                                                                       |
| $\angle C_1' - C_1' - C_1'$ | 2.91547                   | 2.11223                   | 4.1633                    | -15.55033<br>$C_1'$              | 5                                                        | -14.82575<br>$C_1'$              | 1                                                        | 0.87495         | 0.91771         | 0.75  | 1                         | 0.75  | 1.04887 | 0             |                            |                            |                            | 110.76                           |                                                                                                            |
| $\angle C_1' - C_1' - H_1$  | 2.91547                   | 2.09711                   | 4.1633                    | -15.55033<br>$C_1'$              | 5                                                        | -14.82575<br>$C_1'$              | 1                                                        | 0.87495         | 0.91771         | 0.75  | 1                         | 0.75  | 1.04887 | 0             |                            |                            |                            | 111.27                           | 111.4<br>(isobutane)                                                                                       |
| $\angle C_1' - C_1' - C_1'$ | 2.90327                   | 2.90327                   | 4.7938                    | -15.55033<br>$C_1'$              | 5                                                        | -14.82575<br>$C_1'$              | 1                                                        | 0.87495         | 0.91771         | 0.75  | 1                         | 0.75  | 1.04887 | -1.85836      |                            |                            |                            | 111.27                           | 111.4<br>(isobutane)                                                                                       |
| $\angle C_1' - C_1' - C_1'$ |                           |                           |                           |                                  |                                                          |                                  |                                                          |                 |                 |       |                           |       |         |               |                            | 72.50                      |                            | 107.50                           |                                                                                                            |

# ALKENYL HALIDES ( $C_n H_{2n-m} X_m$ , $n = 3, 4, 5 \dots \infty$ $m = 1, 2, 3 \dots \infty$ )

The branched-chain alkenyl halides,  $C_n H_{2n+2-m} X_m$  with  $X = F, Cl, Br, I$ , may comprise alkyl and alkenyl functional groups wherein at least one  $H$  is replaced by a halogen atom. In the case that a halogen atom replaces an alkyl  $H$ , the  $C-X$  bond comprises the alkyl-halogen functional groups given in their respective sections. The alkenyl halogen  $C-X$  bond comprises a separate functional group for each case of  $X$  bonding to the  $C=C$ -bond functional group given in the Alkenes section. In addition the  $CH$  group of the moiety  $XCH=C$  comprises a functional group unique to alkenyl halides. The straight and branched-chain alkenes,  $C_n H_{2n}$ , comprise at least one carbon-carbon double bond comprising a functional group that is solved equivalently to the double bond of ethylene. The double bond may be bound to one, two, three, or four carbon single bonds that substitute for the hydrogen atoms of ethylene. The three distinct functional groups given in the Alkenes section are  $C$  vinyl single bond to  $-C(C)=C$ ,  $C$  vinyl single bond to  $-C(H)=C$ , and  $C$  vinyl single bond to  $-C(C)=CH_2$ . In addition,  $CH_2$  of the  $-C=CH_2$  moiety is also an alkene functional group solved in the Alkenes section.

Consider the case where  $X = Cl$  substitutes for a carbon single bond or a hydrogen atom. Based on the condition of energy matching of the orbital, any magnetic energy due to unpaired electrons in the constituent fragments, and differences in oscillation in the transition state, two distinct  $C-Cl$  functional groups can be identified:  $Cl$  vinyl single bond to  $-C(C)=C$  and  $Cl$  vinyl single bond to  $-C(H)=C$ . The alkenyl-halide  $CH$  group is equivalent to that solved in the Hydrogen Carbide ( $CH$ ) section except that  $\Delta E_{H_2MO}(AO/HO) = -1.13379 \text{ eV}$  in order to energy match to the  $C-Cl$  and  $C=C$  bonds.

The alkyl portion of the alkenyl halide may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in alkene halides are equivalent to those in branched-chain alkanes.

$E_T(\text{atom} - \text{atom}, msp^3.AO)$  of the  $C = C$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  atoms to the MO is equivalent to that of ethylene,  $-2.26759 \text{ eV}$ , given by Eq. (14.247).  $E_T(\text{atom} - \text{atom}, msp^3.AO)$  of each  $C - C$ -bond MO in Eq. (15.52) is  $-1.85836 \text{ eV}$  or  $-1.44915 \text{ eV}$  based on the energy match between the  $C2sp^3$  HOs  
 5 corresponding to the energy contributions equivalent to those of methylene,  $-0.92918 \text{ eV}$  (Eq. (14.513), or methyl,  $-0.72457 \text{ eV}$  (Eq. (14.151)), groups, respectively.

The solution of each  $C - X$  functional group comprises the hybridization of the  $2s$  and  $2p$  AOs of the  $C$  atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the  $X$  AO to form a MO permits each participating  
 10 orbital to decrease in radius and energy. The alkenyl  $C - X$ -bond functional groups comprise single bonds and are equivalent to those of the corresponding alkyl halides except that the halogen AO and the  $C - X$ -bond MO are each energy matched to the alkene  $C2sp^3$  HO. In alkenyl halides with  $X = Cl, Br, \text{ or } I$ , the energy of the halogen atom is less than the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). Thus,  $c_2$  in Eq.  
 15 (15.52) is one, and the energy matching condition is determined by the  $C_2$  parameter. For example, the hybridization factor  $C_2$  of Eq. (15.52) for the alkenyl  $C - Cl$ -bond MO given by Eq. (15.111) is  $C_2(C2sp^3HO \text{ to } Cl) = 0.81317$ .

$E_T(\text{atom} - \text{atom}, msp^3.AO)$  of the alkenyl  $C - Cl$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $Cl$  atoms to the MO is  $-0.72457 \text{ eV}$  for the  $Cl$  vinyl single  
 20 bond to  $-C(H) = C - Cl$  group and  $-0.92918 \text{ eV}$  for the  $Cl$  vinyl single bond to  $-C(C) = C - Cl$  group. It is based on the energy match between the  $Cl$  atom and the  $C2sp^3$  HO of an unsubstituted vinyl group and a substituted vinyl group given by Eqs. (14.151) and (14.513), respectively.

The symbols of the functional groups of branched-chain alkenyl chlorides are given in  
 25 Table 15.51. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkenyl chlorides are given in Tables 15.52, 15.53, and 15.54, respectively. The total energy of each branched-chain alkenyl chloride given in Table 15.55 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.54 corresponding to functional-group composition of the molecule.

The bond angle parameters of branched-chain alkenyl chlorides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.111) are given in Table 15.56.

Table 15.51. The symbols of functional groups of branched-chain alkenyl chlorides.

| Functional Group                    | Group Symbol      |
|-------------------------------------|-------------------|
| Cl vinyl single bond to $-C(H)=C$   | $C-Cl$ (i)        |
| Cl vinyl single bond to $-C(C)=C$   | $C-Cl$ (ii)       |
| CC double bond                      | $C=C$             |
| C vinyl single bond to $-C(C)=C$    | $C-C$ (i)         |
| C vinyl single bond to $-C(H)=C$    | $C-C$ (ii)        |
| C vinyl single bond to $-C(C)=CH_2$ | $C-C$ (iii)       |
| CH (alkenyl halide)                 | $C-H$ (i)         |
| $CH_2$ alkenyl group                | $C-H (CH_2)$ (i)  |
| $CH_3$ group                        | $C-H (CH_3)$      |
| $CH_2$ alkyl group                  | $C-H (CH_2)$ (ii) |
| CH (alkyl)                          | $C-H$ (ii)        |
| CC bond (n-C)                       | $C-C$ (a)         |
| CC bond (iso-C)                     | $C-C$ (b)         |
| CC bond (tert-C)                    | $C-C$ (c)         |
| CC (iso to iso-C)                   | $C-C$ (d)         |
| CC (t to t-C)                       | $C-C$ (e)         |
| CC (t to iso-C)                     | $C-C$ (f)         |

Table 1.5.52. The geometrical bond parameters of branched-chain alkyl chlorides and experimental values [1].

| Parameter                      | C-Cl (i)<br>Group                                           | C-Cl (ii)<br>Group                                          | C-Cl (iii)<br>Group                                                           | C-H (i)<br>Group    | C-H (ii)<br>Group          | C-H (iii)<br>Group         | C-H (CH <sub>3</sub> )<br>Group                       | C-H (CH <sub>3</sub> )<br>Group | C-H (CH <sub>3</sub> )<br>Group                 | C-H (i)<br>Group                                | C-H (ii)<br>Group    | C-H (iii)<br>Group                      | C-C (a)<br>Group                        | C-C (b)<br>Group                        | C-C (c)<br>Group                        | C-C (d)<br>Group                        | C-C (e)<br>Group                        | C-C (f)<br>Group                        |
|--------------------------------|-------------------------------------------------------------|-------------------------------------------------------------|-------------------------------------------------------------------------------|---------------------|----------------------------|----------------------------|-------------------------------------------------------|---------------------------------|-------------------------------------------------|-------------------------------------------------|----------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|
| $\sigma$ (Å)                   | 2.15818                                                     | 2.19338                                                     | 1.47228                                                                       | 2.04740             | 2.04740                    | 2.04740                    | 1.64010                                               | 1.60061                         | 1.64920                                         | 1.67122                                         | 1.67465              | 2.12499                                 | 2.12499                                 | 2.12499                                 | 2.10725                                 | 2.10725                                 | 2.10725                                 | 2.10725                                 |
| $\sigma^*$ (Å)                 | 1.62912                                                     | 1.64243                                                     | 1.26661                                                                       | 1.43087             | 1.43087                    | 1.43087                    | 1.04566                                               | 1.03299                         | 1.04856                                         | 1.05553                                         | 1.05661              | 1.45744                                 | 1.45744                                 | 1.45744                                 | 1.45164                                 | 1.45164                                 | 1.45164                                 | 1.45164                                 |
| Bond Length<br>$2\sigma^*$ (Å) | 1.72419                                                     | 1.73827                                                     | 1.34032                                                                       | 1.51437             | 1.51437                    | 1.51437                    | 1.10668                                               | 1.09327                         | 1.10974                                         | 1.11713                                         | 1.11827              | 1.54280                                 | 1.54280                                 | 1.54280                                 | 1.53635                                 | 1.53635                                 | 1.53635                                 | 1.53635                                 |
| Exp. Bond<br>Length<br>(Å)     | 1.730<br>(vinyl chloride)<br>1.73<br>(1,1-dichloroethylene) | 1.730<br>(vinyl chloride)<br>1.73<br>(1,1-dichloroethylene) | 1.342<br>(2-methylpropane)<br>1.346<br>(2-butene)<br>1.349<br>(1,3-butadiene) | 1.508<br>(2-butene) | 1.508<br>(2-methylpropane) | 1.508<br>(2-methylpropane) | 1.10<br>(2-methylpropane)<br>1.108<br>(1,3-butadiene) | 1.09<br>(vinyl chloride)        | 1.107<br>(C-H propane)<br>1.117<br>(C-H butane) | 1.107<br>(C-H propane)<br>1.117<br>(C-H butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $h, \sigma$ (Å)                | 1.41552                                                     | 1.45403                                                     | 0.75055                                                                       | 1.46439             | 1.46439                    | 1.46439                    | 1.26354                                               | 1.22665                         | 1.27295                                         | 1.29569                                         | 1.29924              | 1.54616                                 | 1.54616                                 | 1.54616                                 | 1.52750                                 | 1.52750                                 | 1.52750                                 | 1.52750                                 |
| $\sigma$                       | 0.75486                                                     | 0.74874                                                     | 0.86030                                                                       | 0.69887             | 0.69887                    | 0.69887                    | 0.63756                                               | 0.64537                         | 0.63580                                         | 0.63159                                         | 0.63095              | 0.68600                                 | 0.68600                                 | 0.68600                                 | 0.68888                                 | 0.68888                                 | 0.68888                                 | 0.68888                                 |



Table 15.53. The MO to HO intercept geometrical bond parameters of branched-chain alkyl chlorides.  $R, R', R''$  are H or alkyl groups.  $E_p$  is  $E_p(\text{atom} - \text{atom}, \text{mp}, \text{AO})$ .

| Bond                               | Atom  | $E_p$<br>(eV)<br>Bond 1 | $E_p$<br>(eV)<br>Bond 2 | $E_p$<br>(eV)<br>Bond 3 | $E_p$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>(eV) | $r_{\text{bond}}$<br>(Å) | $r_{\text{bond}}$<br>(Å) | $E_p(2sp^3)$<br>(eV)<br>Final | $\theta^*$<br>(°) | $\theta_1$<br>(°) | $\theta_2$<br>(°) | $d_1$<br>(Å) | $d_2$<br>(Å) |
|------------------------------------|-------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------------|--------------------------|--------------------------|-------------------------------|-------------------|-------------------|-------------------|--------------|--------------|
| $C_1 = C_1(C) - H(CH)(H)$          | $C_1$ | -1.34946                | -0.72457                | 0                       | 0                       | -153.47406                    | 0.91771                  | 0.81549                  | -16.68412                     | 76.99             | 103.01            | 40.53             | 1.21653      | 0.18354      |
| $-C_8 = C_1(H)C_1$                 | $C_1$ | -1.13379                | -0.72457                | 0                       | 0                       | -153.47406                    | 0.91771                  | 0.81549                  | -16.68412                     | 79.43             | 100.57            | 34.49             | 1.77872      | 0.14960      |
| $(C_1 - C_1)(H)$                   | $C_1$ | -0.72457                | 0                       | 0                       | 0                       |                               | 1.05158                  | 0.87495                  | -15.50533                     | 85.36             | 94.64             | 38.03             | 1.69955      | 0.07083      |
| $-C_8 = C_1(C)C_1$                 | $C_1$ | 1.13379                 | -0.46459                | -0.92918                | 0                       | -154.14326                    | 0.91771                  | 0.78405                  | -17.53532                     | 72.17             | 107.83            | 30.88             | 1.88253      | 0.24010      |
| $(C_1 - C_1)(H)$                   | $C_1$ | -0.46459                | 0                       | 0                       | 0                       |                               | 1.05158                  | 0.88983                  | -15.25034                     | 83.62             | 96.38             | 37.46             | 1.74125      | 0.09882      |
| $-C_8 = C_1(C)C_1$                 | $C_1$ | -1.13380                | -0.92918                | 0                       | 0                       | -153.67867                    | 0.91771                  | 0.80561                  | -16.88873                     | 127.61            | 52.39             | 38.24             | 0.77492      | 0.49168      |
| $C_1(H)C_1 = C_1H_2$               | $C_1$ | -1.13380                | 0                       | 0                       | 0                       | -152.74949                    | 0.91771                  | 0.82552                  | -15.95955                     | 129.84            | 50.16             | 60.70             | 0.72040      | 0.54620      |
| $C_1(C)C_1 = C_1H_2$               | $C_1$ | -1.13380                | -0.72457                | -0.72457                | 0                       | -154.19863                    | 0.91771                  | 0.78155                  | -17.40869                     | 126.39            | 53.61             | 56.95             | 0.80289      | 0.46371      |
| $R_1C_1H_2 - C_1(C) = C$           | $C_1$ | -1.13380                | -0.72457                | -0.72457                | 0                       | -154.19863                    | 0.91771                  | 0.78155                  | -17.40869                     | 60.88             | 119.12            | 27.79             | 1.81127      | 0.38039      |
| $(C_1 - C_1)(H)$                   | $C_1$ | -0.72457                | -0.92918                | 0                       | 0                       | -153.26945                    | 0.91771                  | 0.82562                  | -16.47951                     | 67.40             | 112.60            | 31.36             | 1.74821      | 0.31754      |
| $R_1C_1H_2 - C_1(C) = CH_2$        | $C_1$ | -1.13380                | -0.92918                | 0                       | 0                       | -153.67866                    | 0.91771                  | 0.80561                  | -16.88873                     | 64.57             | 115.43            | 22.79             | 1.77684      | 0.34596      |
| $(C_1 - C_1)(H)$                   | $C_1$ | -0.92918                | -0.92918                | 0                       | 0                       | -153.47405                    | 0.91771                  | 0.81549                  | -16.68411                     | 65.99             | 114.01            | 30.38             | 1.76270      | 0.33185      |
| $R_1C_1H_2 - C_1(H) = C$           | $C_1$ | -1.13380                | 0                       | 0                       | 0                       | -152.74949                    | 0.91771                  | 0.82552                  | -15.95955                     | 77.15             | 102.85            | 41.13             | 1.23331      | 0.18965      |
| $(C_1 - C_1)(H)$                   | $C_1$ | -0.92918                | 0                       | 0                       | 0                       | -152.54487                    | 0.91771                  | 0.80559                  | -15.75493                     | 71.49             | 102.51            | 41.48             | 1.23364      | 0.18708      |
| $C_1 - H(CH_2)(H)$                 | $C_1$ | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                    | 0.91771                  | 0.81549                  | -16.68412                     | 68.47             | 111.53            | 35.84             | 1.35466      | 0.29933      |
| $C_1 - H(CH_2)(H)$                 | $C_1$ | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                    | 0.91771                  | 0.77247                  | -17.41330                     | 61.10             | 118.90            | 31.37             | 1.42088      | 0.37326      |
| $H_1C_1C_1H_2 - C_1(C) = C$        | $C_1$ | -0.92918                | 0                       | 0                       | 0                       | -153.54487                    | 0.91771                  | 0.80539                  | -15.75493                     | 63.82             | 116.18            | 30.08             | 1.83879      | 0.38106      |
| $H_1C_1C_1H_2 - C_1(C) = C$        | $C_1$ | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                    | 0.91771                  | 0.81549                  | -16.68412                     | 56.41             | 123.59            | 26.06             | 1.90890      | 0.45117      |
| $R - H_1C_1C_1(H_1C_1 - R)HCH_2 -$ | $C_1$ | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                    | 0.91771                  | 0.77247                  | -17.41330                     | 48.30             | 131.70            | 21.90             | 1.97162      | 0.51388      |
| $(C_1 - C_1)(H)$                   | $C_1$ | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -154.71860                    | 0.91771                  | 0.75889                  | -17.52866                     | 48.21             | 131.79            | 21.74             | 1.95734      | 0.50570      |
| $R - H_1C_1C_1(H_1C_1 - R)HCH_2 -$ | $C_1$ | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                    | 0.91771                  | 0.77247                  | -17.41330                     | 48.30             | 131.70            | 21.90             | 1.97162      | 0.51388      |
| $(C_1 - C_1)(H)$                   | $C_1$ | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -154.51399                    | 0.91771                  | 0.76765                  | -17.52866                     | 50.04             | 129.96            | 22.66             | 1.94462      | 0.49298      |
| $R - H_1C_1C_1(H_1C_1 - R)HCH_2 -$ | $C_1$ | -0.72457                | -0.72457                | -0.92918                | 0                       | -154.19863                    | 0.91771                  | 0.78155                  | -17.40869                     | 52.78             | 127.22            | 24.04             | 1.92443      | 0.47279      |
| $(C_1 - C_1)(H)$                   | $C_1$ | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.51399                    | 0.91771                  | 0.76765                  | -17.52866                     | 50.04             | 129.96            | 22.66             | 1.94462      | 0.49298      |

Table 15.54 The energy parameters (eV) of functional groups of branched-chain alkanyl chlorides.

[illegible]

T-41a, 15.55. The total bond energies of branched-chain alkene chlorides calculated using the functional group composition and the energies of Table 15.54 compared to the experimental values [21].

Table 15.55. The bond energies of branched-chain alkyl chlorides calculated using the functional group composition and the energies of Table 15.54 compared to the experimental values [2].

| Formula                          | Name            | C—C bond energies compared to the experimental values [2] |          |         |         |           |          |         |                     |                     |                      |         |         |         |         |         |          | Experimental Total Bond Energy (kJ/mol) | Relative Error |
|----------------------------------|-----------------|-----------------------------------------------------------|----------|---------|---------|-----------|----------|---------|---------------------|---------------------|----------------------|---------|---------|---------|---------|---------|----------|-----------------------------------------|----------------|
|                                  |                 | C—Cl (f)                                                  | C—Cl (g) | C—C (f) | C—C (g) | C—C (iii) | C—C (ii) | C—C (i) | CH <sub>2</sub> (f) | CH <sub>3</sub> (i) | CH <sub>2</sub> (ii) | C—C (a) | C—C (b) | C—C (c) | C—C (d) | C—C (e) |          |                                         |                |
| C <sub>3</sub> H <sub>7</sub> Cl | Chloroethane    | 1                                                         | 0        | 1       | 0       | 0         | 1        | 1       | 0                   | 0                   | 0                    | 0       | 0       | 0       | 0       | 0       | 22.595   | 0.00170                                 |                |
| C <sub>4</sub> H <sub>9</sub> Cl | 2-Chloropropane | 0                                                         | 1        | 1       | 0       | 0         | 1        | 1       | 0                   | 0                   | 0                    | 0       | 0       | 0       | 0       | 0       | 35.02984 | 0.00071                                 |                |

Table 15.56. The bond angle parameters of branched-chain alkeryl chlorides and experimental values [1]. In the calculation of  $\theta_i$ , the parameters from the preceding angle were used.  $E_i$  is  $E_i \left( atom, nsp^i, AO \right)$ .

| Atom of Angle | 2c <sup>1</sup><br>Bond 1<br>(a <sub>1</sub> ) | 2c <sup>2</sup><br>Bond 2<br>(a <sub>2</sub> ) | 2c <sup>3</sup><br>Central<br>Atom<br>(a <sub>3</sub> ) | F <sub>2c</sub><br>Atom 1<br>(F <sub>2c</sub> ) | F <sub>2c</sub><br>Atom 2<br>(F <sub>2c</sub> ) | Hybridization<br>Designation<br>(Table 15.3.A) | F <sub>2c</sub><br>Atom 2<br>(F <sub>2c</sub> ) | Hybridization<br>Designation<br>(Table 15.3.A) | c <sub>1</sub> | c <sub>2</sub> | c <sub>3</sub> | c <sub>4</sub> | c <sub>5</sub> | c <sub>6</sub> | c <sub>7</sub> | c <sub>8</sub> | c <sub>9</sub> | c <sub>10</sub> | c <sub>11</sub> | c <sub>12</sub> | c <sub>13</sub> | c <sub>14</sub> | c <sub>15</sub> | c <sub>16</sub> | c <sub>17</sub> | c <sub>18</sub> | c <sub>19</sub> | c <sub>20</sub> | c <sub>21</sub> | c <sub>22</sub> | c <sub>23</sub> | c <sub>24</sub> | c <sub>25</sub> | c <sub>26</sub> | c <sub>27</sub> | c <sub>28</sub> | c <sub>29</sub> | c <sub>30</sub> | c <sub>31</sub> | c <sub>32</sub> | c <sub>33</sub> | c <sub>34</sub> | c <sub>35</sub> | c <sub>36</sub> | c <sub>37</sub> | c <sub>38</sub> | c <sub>39</sub> | c <sub>40</sub> | c <sub>41</sub> | c <sub>42</sub> | c <sub>43</sub> | c <sub>44</sub> | c <sub>45</sub> | c <sub>46</sub> | c <sub>47</sub> | c <sub>48</sub> | c <sub>49</sub> | c <sub>50</sub> | c <sub>51</sub> | c <sub>52</sub> | c <sub>53</sub> | c <sub>54</sub> | c <sub>55</sub> | c <sub>56</sub> | c <sub>57</sub> | c <sub>58</sub> | c <sub>59</sub> | c <sub>60</sub> | c <sub>61</sub> | c <sub>62</sub> | c <sub>63</sub> | c <sub>64</sub> | c <sub>65</sub> | c <sub>66</sub> | c <sub>67</sub> | c <sub>68</sub> | c <sub>69</sub> | c <sub>70</sub> | c <sub>71</sub> | c <sub>72</sub> | c <sub>73</sub> | c <sub>74</sub> | c <sub>75</sub> | c <sub>76</sub> | c <sub>77</sub> | c <sub>78</sub> | c <sub>79</sub> | c <sub>80</sub> | c <sub>81</sub> | c <sub>82</sub> | c <sub>83</sub> | c <sub>84</sub> | c <sub>85</sub> | c <sub>86</sub> | c <sub>87</sub> | c <sub>88</sub> | c <sub>89</sub> | c <sub>90</sub> | c <sub>91</sub> | c <sub>92</sub> | c <sub>93</sub> | c <sub>94</sub> | c <sub>95</sub> | c <sub>96</sub> | c <sub>97</sub> | c <sub>98</sub> | c <sub>99</sub> | c <sub>100</sub> | c <sub>101</sub> | c <sub>102</sub> | c <sub>103</sub> | c <sub>104</sub> | c <sub>105</sub> | c <sub>106</sub> | c <sub>107</sub> | c <sub>108</sub> | c <sub>109</sub> | c <sub>110</sub> | c <sub>111</sub> | c <sub>112</sub> | c <sub>113</sub> | c <sub>114</sub> | c <sub>115</sub> | c <sub>116</sub> | c <sub>117</sub> | c <sub>118</sub> | c <sub>119</sub> | c <sub>120</sub> | c <sub>121</sub> | c <sub>122</sub> | c <sub>123</sub> | c <sub>124</sub> | c <sub>125</sub> | c <sub>126</sub> | c <sub>127</sub> | c <sub>128</sub> | c <sub>129</sub> | c <sub>130</sub> | c <sub>131</sub> | c <sub>132</sub> | c <sub>133</sub> | c <sub>134</sub> | c <sub>135</sub> | c <sub>136</sub> | c <sub>137</sub> | c <sub>138</sub> | c <sub>139</sub> | c <sub>140</sub> | c <sub>141</sub> | c <sub>142</sub> | c <sub>143</sub> | c <sub>144</sub> | c <sub>145</sub> | c <sub>146</sub> | c <sub>147</sub> | c <sub>148</sub> | c <sub>149</sub> | c <sub>150</sub> | c <sub>151</sub> | c <sub>152</sub> | c <sub>153</sub> | c <sub>154</sub> | c <sub>155</sub> | c <sub>156</sub> | c <sub>157</sub> | c <sub>158</sub> | c <sub>159</sub> | c <sub>160</sub> | c <sub>161</sub> | c <sub>162</sub> | c <sub>163</sub> | c <sub>164</sub> | c <sub>165</sub> | c <sub>166</sub> | c <sub>167</sub> | c <sub>168</sub> | c <sub>169</sub> | c <sub>170</sub> | c <sub>171</sub> | c <sub>172</sub> | c <sub>173</sub> | c <sub>174</sub> | c <sub>175</sub> | c <sub>176</sub> | c <sub>177</sub> | c <sub>178</sub> | c <sub>179</sub> | c <sub>180</sub> | c <sub>181</sub> | c <sub>182</sub> | c <sub>183</sub> | c <sub>184</sub> | c <sub>185</sub> | c <sub>186</sub> | c <sub>187</sub> | c <sub>188</sub> | c <sub>189</sub> | c <sub>190</sub> | c <sub>191</sub> | c <sub>192</sub> | c <sub>193</sub> | c <sub>194</sub> | c <sub>195</sub> | c <sub>196</sub> | c <sub>197</sub> | c <sub>198</sub> | c <sub>199</sub> | c <sub>200</sub> | c <sub>201</sub> | c <sub>202</sub> | c <sub>203</sub> | c <sub>204</sub> | c <sub>205</sub> | c <sub>206</sub> | c <sub>207</sub> | c <sub>208</sub> | c <sub>209</sub> | c <sub>210</sub> | c <sub>211</sub> | c <sub>212</sub> | c <sub>213</sub> | c <sub>214</sub> | c <sub>215</sub> | c <sub>216</sub> | c <sub>217</sub> | c <sub>218</sub> | c <sub>219</sub> | c <sub>220</sub> | c <sub>221</sub> | c <sub>222</sub> | c <sub>223</sub> | c <sub>224</sub> | c <sub>225</sub> | c <sub>226</sub> | c <sub>227</sub> | c <sub>228</sub> | c <sub>229</sub> | c <sub>230</sub> | c <sub>231</sub> | c <sub>232</sub> | c <sub>233</sub> | c <sub>234</sub> | c <sub>235</sub> | c <sub>236</sub> | c <sub>237</sub> | c <sub>238</sub> | c <sub>239</sub> | c <sub>240</sub> | c <sub>241</sub> | c <sub>242</sub> | c <sub>243</sub> | c <sub>244</sub> | c <sub>245</sub> | c <sub>246</sub> | c <sub>247</sub> | c <sub>248</sub> | c <sub>249</sub> | c <sub>250</sub> | c <sub>251</sub> | c <sub>252</sub> | c <sub>253</sub> | c <sub>254</sub> | c <sub>255</sub> | c <sub>256</sub> | c <sub>257</sub> | c <sub>258</sub> | c <sub>259</sub> | c <sub>260</sub> | c <sub>261</sub> | c <sub>262</sub> | c <sub>263</sub> | c <sub>264</sub> | c <sub>265</sub> | c <sub>266</sub> | c <sub>267</sub> | c <sub>268</sub> | c <sub>269</sub> | c <sub>270</sub> | c <sub>271</sub> | c <sub>272</sub> | c <sub>273</sub> | c <sub>274</sub> | c <sub>275</sub> | c <sub>276</sub> | c <sub>277</sub> | c <sub>278</sub> | c <sub>279</sub> | c <sub>280</sub> | c <sub>281</sub> | c <sub>282</sub> | c <sub>283</sub> | c <sub>284</sub> | c <sub>285</sub> | c <sub>286</sub> | c <sub>287</sub> | c <sub>288</sub> | c <sub>289</sub> | c <sub>290</sub> | c <sub>291</sub> | c <sub>292</sub> | c <sub>293</sub> | c <sub>294</sub> | c <sub>295</sub> | c <sub>296</sub> | c <sub>297</sub> | c <sub>298</sub> | c <sub>299</sub> | c <sub>300</sub> | c <sub>301</sub> | c <sub>302</sub> | c <sub>303</sub> | c <sub>304</sub> | c <sub>305</sub> | c <sub>306</sub> | c <sub>307</sub> | c <sub>308</sub> | c <sub>309</sub> | c <sub>310</sub> | c <sub>311</sub> | c <sub>312</sub> | c <sub>313</sub> | c <sub>314</sub> | c <sub>315</sub> | c <sub>316</sub> | c <sub>317</sub> | c <sub>318</sub> | c <sub>319</sub> | c <sub>320</sub> | c <sub>321</sub> | c <sub>322</sub> | c <sub>323</sub> | c <sub>324</sub> | c <sub>325</sub> | c <sub>326</sub> | c <sub>327</sub> | c <sub>328</sub> | c <sub>329</sub> | c <sub>330</sub> | c <sub>331</sub> | c <sub>332</sub> | c <sub>333</sub> | c <sub>334</sub> | c <sub>335</sub> | c <sub>336</sub> | c <sub>337</sub> | c <sub>338</sub> | c <sub>339</sub> | c <sub>340</sub> | c <sub>341</sub> | c <sub>342</sub> | c <sub>343</sub> | c <sub>344</sub> | c <sub>345</sub> | c <sub>346</sub> | c <sub>347</sub> | c <sub>348</sub> | c <sub>349</sub> | c <sub>350</sub> | c <sub>351</sub> | c <sub>352</sub> | c <sub>353</sub> | c <sub>354</sub> | c <sub>355</sub> | c <sub>356</sub> | c <sub>357</sub> | c <sub>358</sub> | c <sub>359</sub> | c <sub>360</sub> | c <sub>361</sub> | c <sub>362</sub> | c <sub>363</sub> | c <sub>364</sub> | c <sub>365</sub> | c <sub>366</sub> | c <sub>367</sub> | c <sub>368</sub> | c <sub>369</sub> | c <sub>370</sub> | c <sub>371</sub> | c <sub>372</sub> | c <sub>373</sub> | c <sub>374</sub> | c <sub>375</sub> | c <sub>376</sub> | c <sub>377</sub> | c <sub>378</sub> | c <sub>379</sub> | c <sub>380</sub> | c <sub>381</sub> | c <sub>382</sub> | c <sub>383</sub> | c <sub>384</sub> | c <sub>385</sub> | c <sub>386</sub> | c <sub>387</sub> | c <sub>388</sub> | c <sub>389</sub> | c <sub>390</sub> | c <sub>391</sub> | c <sub>392</sub> | c <sub>393</sub> | c <sub>394</sub> | c <sub>395</sub> | c <sub>396</sub> | c <sub>397</sub> | c <sub>398</sub> | c <sub>399</sub> | c <sub>400</sub> | c <sub>401</sub> | c <sub>402</sub> | c <sub>403</sub> | c <sub>404</sub> | c <sub>405</sub> | c <sub>406</sub> | c <sub>407</sub> | c <sub>408</sub> | c <sub>409</sub> | c <sub>410</sub> | c <sub>411</sub> | c <sub>412</sub> | c <sub>413</sub> | c <sub>414</sub> | c <sub>415</sub> | c <sub>416</sub> | c <sub>417</sub> | c <sub>418</sub> | c <sub>419</sub> | c <sub>420</sub> | c <sub>421</sub> | c <sub>422</sub> | c <sub>423</sub> | c <sub>424</sub> | c <sub>425</sub> | c <sub>426</sub> | c <sub>427</sub> | c <sub>428</sub> | c <sub>429</sub> | c <sub>430</sub> | c <sub>431</sub> | c <sub>432</sub> | c <sub>433</sub> | c <sub>434</sub> | c <sub>435</sub> | c <sub>436</sub> | c <sub>437</sub> | c <sub>438</sub> | c <sub>439</sub> | c <sub>440</sub> | c <sub>441</sub> | c <sub>442</sub> | c <sub>443</sub> | c <sub>444</sub> | c <sub>445</sub> | c <sub>446</sub> | c <sub>447</sub> | c <sub>448</sub> | c <sub>449</sub> | c <sub>450</sub> | c <sub>451</sub> | c <sub>452</sub> | c <sub>453</sub> | c <sub>454</sub> | c <sub>455</sub> | c <sub>456</sub> | c <sub>457</sub> | c <sub>458</sub> | c <sub>459</sub> | c <sub>460</sub> | c <sub>461</sub> | c <sub>462</sub> | c <sub>463</sub> | c <sub>464</sub> | c <sub>465</sub> | c <sub>466</sub> | c <sub>467</sub> | c <sub>468</sub> | c <sub>469</sub> | c <sub>470</sub> | c <sub>471</sub> | c <sub>472</sub> | c <sub>473</sub> | c <sub>474</sub> | c <sub>475</sub> | c <sub>476</sub> | c <sub>477</sub> | c <sub>478</sub> | c <sub>479</sub> | c <sub>480</sub> | c <sub>481</sub> | c <sub>482</sub> | c <sub>483</sub> | c <sub>484</sub> | c <sub>485</sub> | c <sub>486</sub> | c <sub>487</sub> | c <sub>488</sub> | c <sub>489</sub> | c <sub>490</sub> | c <sub>491</sub> | c <sub>492</sub> | c <sub>493</sub> | c <sub>494</sub> | c <sub>495</sub> | c <sub>496</sub> | c <sub>497</sub> | c <sub>498</sub> | c <sub>499</sub> | c <sub>500</sub> | c <sub>501</sub> | c <sub>502</sub> | c <sub>503</sub> | c <sub>504</sub> | c 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<sub>557</sub> | c <sub>558</sub> | c <sub>559</sub> | c <sub>560</sub> | c <sub>561</sub> | c <sub>562</sub> | c <sub>563</sub> | c <sub>564</sub> | c <sub>565</sub> | c <sub>566</sub> | c <sub>567</sub> | c <sub>568</sub> | c <sub>569</sub> | c <sub>570</sub> | c <sub>571</sub> | c <sub>572</sub> | c <sub>573</sub> | c <sub>574</sub> | c <sub>575</sub> | c <sub>576</sub> | c <sub>577</sub> | c <sub>578</sub> | c <sub>579</sub> | c <sub>580</sub> | c <sub>581</sub> | c <sub>582</sub> | c <sub>583</sub> | c <sub>584</sub> | c <sub>585</sub> | c <sub>586</sub> | c <sub>587</sub> | c <sub>588</sub> | c <sub>589</sub> | c <sub>590</sub> | c <sub>591</sub> | c <sub>592</sub> | c <sub>593</sub> | c <sub>594</sub> | c <sub>595</sub> | c <sub>596</sub> | c <sub>597</sub> | c <sub>598</sub> | c <sub>599</sub> | c <sub>600</sub> | c <sub>601</sub> | c <sub>602</sub> | c <sub>603</sub> | c <sub>604</sub> | c <sub>605</sub> | c <sub>606</sub> | c <sub>607</sub> | c <sub>608</sub> | c <sub>609</sub> | c <sub>610</sub> | c <sub>611</sub> | c <sub>612</sub> | c <sub>613</sub> | c <sub>614</sub> | c <sub>615</sub> | c <sub>616</sub> | c <sub>617</sub> | c <sub>618</sub> | c <sub>619</sub> | c <sub>620</sub> | c <sub>621</sub> | c <sub>622</sub> | c <sub>623</sub> | c <sub>624</sub> | c <sub>625</sub> | c <sub>626</sub> | c <sub>627</sub> | c <sub>628</sub> | c <sub>629</sub> | c <sub>630</sub> | c <sub>631</sub> | c <sub>632</sub> | c <sub>633</sub> | c <sub>634</sub> | c <sub>635</sub> | c <sub>636</sub> | c <sub>637</sub> | c <sub>638</sub> | c <sub>639</sub> | c <sub>640</sub> | c <sub>641</sub> | c <sub>642</sub> | c <sub>643</sub> | c <sub>644</sub> | c <sub>645</sub> | c <sub>646</sub> | c <sub>647</sub> | c <sub>648</sub> | c <sub>649</sub> | c <sub>650</sub> | c <sub>651</sub> | c <sub>652</sub> | c <sub>653</sub> | c <sub>654</sub> | c <sub>655</sub> | c <sub>656</sub> | c <sub>657</sub> | c <sub>658</sub> | c <sub>659</sub> | c <sub>660</sub> | c <sub>661</sub> | c <sub>662</sub> | c <sub>663</sub> | c <sub>664</sub> | c <sub>665</sub> | c <sub>666</sub> | c <sub>667</sub> | c <sub>668</sub> | c <sub>669</sub> | c <sub>670</sub> | c <sub>671</sub> | c <sub>672</sub> | c <sub>673</sub> | c <sub>674</sub> | c <sub>675</sub> | c <sub>676</sub> | c <sub>677</sub> | c <sub>678</sub> | c <sub>679</sub> | c <sub>680</sub> | c <sub>681</sub> | c <sub>682</sub> | c <sub>683</sub> | c <sub>684</sub> | c <sub>685</sub> | c <sub>686</sub> | c <sub>687</sub> | c <sub>688</sub> | c <sub>689</sub> | c <sub>690</sub> | c <sub>691</sub> | c <sub>692</sub> | c <sub>693</sub> | c <sub>694</sub> | c <sub>695</sub> | c <sub>696</sub> | c <sub>697</sub> | c <sub>698</sub> | c <sub>699</sub> | c <sub>700</sub> | c <sub>701</sub> | c <sub>702</sub> | c <sub>703</sub> | c <sub>704</sub> | c <sub>705</sub> | c <sub>706</sub> | c <sub>707</sub> | c <sub>708</sub> | c <sub>709</sub> | c <sub>710</sub> | c <sub>711</sub> | c <sub>712</sub> | c 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<sub>765</sub> | c <sub>766</sub> | c <sub>767</sub> | c <sub>768</sub> | c <sub>769</sub> | c <sub>770</sub> | c <sub>771</sub> | c <sub>772</sub> | c <sub>773</sub> | c <sub>774</sub> | c <sub>775</sub> | c <sub>776</sub> | c <sub>777</sub> | c <sub>778</sub> | c <sub>779</sub> | c <sub>780</sub> | c <sub>781</sub> | c <sub>782</sub> | c <sub>783</sub> | c <sub>784</sub> | c <sub>785</sub> | c <sub>786</sub> | c <sub>787</sub> | c <sub>788</sub> | c <sub>789</sub> | c <sub>790</sub> | c <sub>791</sub> | c <sub>792</sub> | c <sub>793</sub> | c <sub>794</sub> | c <sub>795</sub> | c <sub>796</sub> | c <sub>797</sub> | c <sub>798</sub> | c <sub>799</sub> | c <sub>800</sub> | c <sub>801</sub> | c <sub>802</sub> | c <sub>803</sub> | c <sub>804</sub> | c <sub>805</sub> | c <sub>806</sub> | c <sub>807</sub> | c <sub>808</sub> | c <sub>809</sub> | c <sub>810</sub> | c <sub>811</sub> | c <sub>812</sub> | c <sub>813</sub> | c <sub>814</sub> | c <sub>815</sub> | c <sub>816</sub> | c <sub>817</sub> | c <sub>818</sub> | c <sub>819</sub> | c <sub>820</sub> | c <sub>821</sub> | c <sub>822</sub> | c <sub>823</sub> | c <sub>824</sub> | c <sub>825</sub> | c <sub>826</sub> | c <sub>827</sub> | c <sub>828</sub> | c <sub>829</sub> | c <sub>830</sub> | c <sub>831</sub> | c <sub>832</sub> | c <sub>833</sub> | c <sub>834</sub> | c <sub>835</sub> | c <sub>836</sub> | c <sub>837</sub> | c <sub>838</sub> | c <sub>839</sub> | c <sub>840</sub> | c <sub>841</sub> | c <sub>842</sub> | c <sub>843</sub> | c <sub>844</sub> | c <sub>845</sub> | c <sub>846</sub> | c <sub>847</sub> | c <sub>848</sub> | c <sub>849</sub> | c <sub>850</sub> | c <sub>851</sub> | c <sub>852</sub> | c <sub>853</sub> | c <sub>854</sub> | c <sub>855</sub> | c <sub>856</sub> | c <sub>857</sub> | c <sub>858</sub> | c <sub>859</sub> | c <sub>860</sub> | c <sub>861</sub> | c <sub>862</sub> | c <sub>863</sub> | c <sub>864</sub> | c <sub>865</sub> | c <sub>866</sub> | c <sub>867</sub> | c <sub>868</sub> | c <sub>869</sub> | c <sub>870</sub> | c <sub>871</sub> | c <sub>872</sub> | c <sub>873</sub> | c <sub>874</sub> | c <sub>875</sub> | c <sub>876</sub> | c <sub>877</sub> | c <sub>878</sub> | c <sub>879</sub> | c <sub>880</sub> | c <sub>881</sub> | c <sub>882</sub> | c <sub>883</sub> | c <sub>884</sub> | c <sub>885</sub> | c <sub>886</sub> | c <sub>887</sub> | c <sub>888</sub> | c <sub>889</sub> | c <sub>890</sub> | c <sub>891</sub> | c <sub>892</sub> | c <sub>893</sub> | c <sub>894</sub> | c <sub>895</sub> | c <sub>896</sub> | c <sub>897</sub> | c <sub>898</sub> | c <sub>899</sub> | c <sub>900</sub> | c <sub>901</sub> | c <sub>902</sub> | c <sub>903</sub> | c <sub>904</sub> | c <sub>905</sub> | c <sub>906</sub> | c <sub>907</sub> | c <sub>908</sub> | c <sub>909</sub> | c <sub>910</sub> | c <sub>911</sub> | c <sub>912</sub> | c <sub>913</sub> | c <sub>914</sub> | c <sub>915</sub> | c <sub>916</sub> | c <sub>917</sub> | c <sub>918</sub> | c <sub>919</sub> | c <sub>920</sub> | c <sub>921</sub> | c <sub>922</sub> | c <sub>923</sub> | c <sub>924</sub> | c <sub>925</sub> | c <sub>926</sub> | c <sub>927</sub> | c <sub>928</sub> | c <sub>929</sub> | c <sub>930</sub> | c <sub>931</sub> | c <sub>932</sub> | c <sub>933</sub> | c <sub>934</sub> | c <sub>935</sub> | c <sub>936</sub> | c <sub>937</sub> | c <sub>938</sub> | c <sub>939</sub> | c <sub>940</sub> | c <sub>941</sub> | c <sub>942</sub> | c <sub>943&lt;/</sub> |
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ALCOHOLS ( $C_nH_{2n+2}O_m$ ,  $n=1,2,3,4,5\ldots\infty$ )

The alkyl alcohols,  $C_nH_{2n+2}O_m$ , comprise an  $OH$  functional group and two types of  $C-O$  functional groups, one for methyl alcohol and the other for general alkyl alcohols. The alkyl portion of the alkyl alcohol may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in alcohols are equivalent to those in branched-chain alkanes.

The  $OH$  functional group was solved in the Hydroxyl Radical ( $OH$ ) section. Each  $C-O$  group is solved by hybridizing the  $2s$  and  $2p$  AOs of the  $C$  atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the  $O$  AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl alcohols, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)) and the  $O$  AO has an energy of  $E(O) = -13.61806 \text{ eV}$ . To meet the equipotential condition of the union of the  $C-O$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the  $C-O$ -bond MO given by Eqs. (15.68) and (15.70) is

$$c_2(C2sp^3HO \text{ to } O) = \frac{E(O)}{E(C, 2sp^3)} c_2(C2sp^3HO) = \frac{-13.61806 \text{ eV}}{-14.63489 \text{ eV}} (0.91771) = 0.85395 \quad (15.114)$$

$E_r(atom - atom, msp^3.AO)$  of the  $C-O$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $O$  atoms to the MO is  $-1.65376 \text{ eV}$  for the  $CH_3-OH$   $C-O$  group. It is based on the energy match between the  $OH$  group and the  $C2sp^3$  HO of a methyl group and is given by the linear combination of  $-0.92918 \text{ eV}$  (Eq. (14.513)) and  $-0.72457 \text{ eV}$  (Eq. (14.151)), respectively. For the alkyl  $C-O$  group,  $E_r(atom - atom, msp^3.AO)$  is  $-1.85836 \text{ eV}$ . It is based on the energy match between the  $O$  AO and the  $C2sp^3$  HO of a methylene group where both energy contributions are given by Eq. (14.513).

The symbols of the functional groups of branched-chain alkyl alcohols are given in Table 15.57. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl alcohols are given in Tables 15.58, 15.59, and 15.60, respectively. The total energy of each alkyl alcohol given in Table 5 15.61 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.60 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl alcohols determined using Eqs. (15.79-15.108) are given in Table 15.62.

Table 15.58. The geometrical bond parameters of alkyl alcohols and experimental values [1].

| Functional Group       | OH Group | Group Symbol            |
|------------------------|----------|-------------------------|
| OH group               |          | OH                      |
| CH <sub>3</sub> OH C-O |          | C-O (i)                 |
| Alkyl C-O              |          | C-O (ii)                |
| CH <sub>3</sub> group  |          | C'-H (CH <sub>3</sub> ) |
| CH <sub>2</sub> group  |          | C-H (CH <sub>2</sub> )  |
| CH                     |          | C-H                     |
| CC bond (n-C)          |          | C'-C (a)                |
| CC bond (iso-C)        |          | C-C (b)                 |
| CC bond (tert-C)       |          | C-C (c)                 |
| CC (iso to iso-C)      |          | C-C (d)                 |
| CC (t to t-C)          |          | C-C (e)                 |
| CC (t to iso-C)        |          | C-C (f)                 |

Table 15.58. The geometrical bond parameters of alkyl alcohols and experimental values [1].

| Parameter              | OH Group                             | C-O (i) Group     | C-O (ii) Group  | C'-H (CH <sub>3</sub> ) Group             | C-H Group         | C-C (a) Group                     | C-C (b) Group                     | C-C (c) Group                     | C-C (d) Group                     | C-C (e) Group                     | C-C (f) Group                     |
|------------------------|--------------------------------------|-------------------|-----------------|-------------------------------------------|-------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| $\alpha$ ( $^\circ$ )  | 1.26430                              | 1.79473           | 1.78255         | 1.67122                                   | 1.67465           | 2.12499                           | 2.12499                           | 2.10725                           | 2.12499                           | 2.10725                           | 2.10725                           |
| $\alpha'$ ( $^\circ$ ) | 0.91808                              | 1.33968           | 1.33512         | 1.04856                                   | 1.05661           | 1.45744                           | 1.45744                           | 1.45164                           | 1.45744                           | 1.45164                           | 1.45164                           |
| Bond Length            |                                      |                   |                 |                                           |                   |                                   |                                   |                                   |                                   |                                   |                                   |
| $2c'$ ( $\text{\AA}$ ) | 0.971651                             | 1.41785           | 1.41303         | 1.10974                                   | 1.11827           | 1.54280                           | 1.54280                           | 1.53635                           | 1.54280                           | 1.53635                           | 1.53635                           |
| Exp. Bond Length       | 0.971 (ethanol)<br>0.9451 (methanol) | 1.4246 (methanol) | 1.431 (ethanol) | 1.107 (C-H propane)<br>1.117 (C-H butane) | 1.122 (isobutane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) |
| $b, c$ ( $^\circ$ )    | 0.86925                              | 1.19429           | 1.18107         | 1.27295                                   | 1.29924           | 1.54616                           | 1.54616                           | 1.52750                           | 1.54616                           | 1.52750                           | 1.52750                           |
| $e$                    | 0.72615                              | 0.74645           | 0.74900         | 0.63580                                   | 0.63095           | 0.68600                           | 0.68600                           | 0.68888                           | 0.68600                           | 0.68888                           | 0.68888                           |

Table 15.59. The MO to HO intercept geometrical bond parameters of alkyl alcohols.  $R, R', R''$  are H or alkyl groups.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{mwp}, AO)$ .

| Bond                       | Atom | $E_T$<br>(eV)<br>Bond 1 | $E_T$<br>(eV)<br>Bond 2 | $E_T$<br>(eV)<br>Bond 3 | $E_T$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>$C_{2sp^3}$<br>(eV) | $r_{\text{mwp}}$<br>( $a_0$ ) | $r_{\text{final}}$<br>( $a_0$ ) | $E_{\text{Coulomb}}$<br>(eV)<br>Final | $E(C_{2sp^3})$<br>(eV)<br>Final | $\theta^*$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | $d_1$<br>( $a_0$ ) | $d_2$<br>( $a_0$ ) |
|----------------------------|------|-------------------------|-------------------------|-------------------------|-------------------------|----------------------------------------------|-------------------------------|---------------------------------|---------------------------------------|---------------------------------|----------------------------|----------------------------|----------------------------|--------------------|--------------------|
| $H_1C-O-H$                 | O    | -0.82688                | 0                       | 0                       | 0                       |                                              | 1.00000                       | 0.86923                         | -15.65263                             |                                 | 115.49                     | 64.51                      | 64.51                      | 0.54405            | 0.37403            |
| $-H_1C-O-H$                | O    | -0.92918                | 0                       | 0                       | 0                       |                                              | 1.00000                       | 0.86359                         | -15.75493                             |                                 | 115.09                     | 64.91                      | 64.12                      | 0.55182            | 0.36625            |
| $H_1C-OH$                  | C    | -0.82688                | 0                       | 0                       | 0                       | -152.44257                                   | 0.91771                       | 0.86923                         | -15.65263                             | -15.46177                       | 96.59                      | 83.41                      | 46.30                      | 1.23986            | 0.09981            |
| $H_1C-OH$                  | O    | -0.82688                | 0                       | 0                       | 0                       |                                              | 1.00000                       | 0.86923                         | -15.65263                             |                                 | 96.59                      | 83.41                      | 46.30                      | 1.23986            | 0.09981            |
| $-H_1C-OH$                 | C    | -0.92918                | -0.92918                | 0                       | 0                       | -153.47405                                   | 0.91771                       | 0.81549                         | -16.68411                             | -16.49325                       | 93.09                      | 86.91                      | 43.59                      | 1.29114            | 0.04398            |
| $-H_1C-OH$                 | O    | -0.92918                | 0                       | 0                       | 0                       |                                              | 1.00000                       | 0.86359                         | -15.75493                             |                                 | 97.20                      | 82.80                      | 46.50                      | 1.22692            | 0.10820            |
| $C-H (CH_3)$               | C    | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                   | 0.91771                       | 0.86359                         | -15.75493                             | -15.56407                       | 77.49                      | 102.51                     | 41.48                      | 1.23564            | 0.18708            |
| $C-H (CH_2)$               | C    | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                   | 0.91771                       | 0.81549                         | -16.68412                             | -16.49325                       | 68.47                      | 111.53                     | 35.84                      | 1.35486            | 0.29933            |
| $C-H (CH)$                 | C    | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                   | 0.91771                       | 0.77247                         | -17.61330                             | -17.42244                       | 61.10                      | 118.90                     | 31.37                      | 1.42988            | 0.37326            |
| $H_1C-C_1H_2CH_3$          | C    | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                   | 0.91771                       | 0.86359                         | -15.75493                             | -15.56407                       | 63.82                      | 116.18                     | 30.08                      | 1.83879            | 0.38106            |
| $H_1C-C_1H_2CH_3$          | C    | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                   | 0.91771                       | 0.81549                         | -16.68412                             | -16.49325                       | 56.41                      | 123.59                     | 26.06                      | 1.90890            | 0.45117            |
| $R-H_1C-C_1(H_2C-R')HCH_2$ | C    | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                   | 0.91771                       | 0.77247                         | -17.61330                             | -17.42244                       | 48.30                      | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| $(C-C (b))$                | C    | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -154.71860                                   | 0.91771                       | 0.75889                         | -17.92866                             | -17.73779                       | 48.21                      | 131.79                     | 21.74                      | 1.95734            | 0.50570            |
| $R-H_1C-C_1(H_2C-R')HCH_2$ | C    | -0.92918                | -0.72457                | -0.92918                | 0                       | -154.40324                                   | 0.91771                       | 0.77247                         | -17.61330                             | -17.42244                       | 48.30                      | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| $(C-C (e))$                | C    | -0.92918                | -0.72457                | -0.92918                | -0.72457                | -154.51399                                   | 0.91771                       | 0.76765                         | -17.92866                             | -17.73779                       | 50.04                      | 129.96                     | 22.66                      | 1.94462            | 0.49298            |
| $R-H_1C-C_1(H_2C-R')HCH_2$ | C    | -0.92918                | -0.72457                | -0.92918                | 0                       | -154.19863                                   | 0.91771                       | 0.78155                         | -17.40869                             | -17.21783                       | 52.78                      | 127.22                     | 24.04                      | 1.92443            | 0.47279            |
| $(C-C (f))$                | C    | -0.92918                | -0.72457                | -0.92918                | -0.72457                | -154.51399                                   | 0.91771                       | 0.76765                         | -17.92866                             | -17.73779                       | 50.04                      | 129.96                     | 22.66                      | 1.94462            | 0.49298            |

Table 15.60. The energy parameters (eV) of functional groups of alkyl alcohols.

| Parameters                | OH Group  | C-O (i) Group | C-O (ii) Group | C-H <sub>3</sub> Group | C-H <sub>2</sub> Group | C-H Group      | C-C (a) Group | C-C (b) Group | C-C (c) Group | C-C (d) Group | C-C (e) Group | C-C (f) Group |
|---------------------------|-----------|---------------|----------------|------------------------|------------------------|----------------|---------------|---------------|---------------|---------------|---------------|---------------|
| $n_1$                     | 1         | 1             | 1              | 2                      | 1                      | 1              | 1             | 1             | 1             | 1             | 1             | 1             |
| $n_2$                     | 0         | 0             | 0              | 1                      | 0                      | 0              | 0             | 0             | 0             | 0             | 0             | 0             |
| $n_3$                     | 0         | 0             | 0              | 0                      | 0                      | 0              | 0             | 0             | 0             | 0             | 0             | 0             |
| $C_1$                     | 0.75      | 0.5           | 0.5            | 0.75                   | 0.75                   | 0.75           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           |
| $C_2$                     | 1         | 1             | 1              | 1                      | 1                      | 1              | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_3$                     | 0.75      | 1             | 1              | 1                      | 1                      | 1              | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_4$                     | 1         | 0.85395       | 0.85395        | 0.91771                | 0.91771                | 0.91771        | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       |
| $C_5$                     | 1         | 0             | 0              | 1                      | 1                      | 1              | 0             | 0             | 0             | 1             | 1             | 0             |
| $C_6$                     | 1         | 2             | 2              | 1                      | 1                      | 1              | 2             | 2             | 2             | 2             | 2             | 2             |
| $C_7$                     | 1         | 0             | 0              | 3                      | 1                      | 1              | 0             | 0             | 0             | 0             | 0             | 0             |
| $C_{100}$                 | 0.75      | 0.5           | 0.5            | 0.75                   | 0.75                   | 0.75           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           |
| $C'_{100}$                | 1         | 1             | 1              | 1                      | 1                      | 1              | 1             | 1             | 1             | 1             | 1             | 1             |
| $V'_p$ (eV)               | -40.92709 | -33.47304     | -33.78820      | -107.32728             | -70.41425              | -35.12015      | -28.79214     | -28.79214     | -29.10112     | -28.79214     | -29.10112     | -29.10112     |
| $V_p$ (eV)                | 14.81988  | 10.15605      | 10.19068       | 38.92728               | 25.78002               | 12.87680       | 9.33552       | 9.33552       | 9.37273       | 9.33552       | 9.37273       | 9.37273       |
| $T$ (eV)                  | 16.18567  | 9.32537       | 9.47749        | 32.53914               | 21.06675               | 10.48582       | 6.77464       | 6.77464       | 6.90500       | 6.77464       | 6.90500       | 6.90500       |
| $V''_m$ (eV)              | -8.09284  | -4.66268      | -4.73874       | -16.26957              | -10.53337              | -5.24291       | -3.38732      | -3.38732      | -3.45250      | -3.38732      | -3.45250      | -3.45250      |
| $E'_{(w, m)}$ (eV)        | -13.6181  | -14.63489     | -14.63489      | -15.56407              | -15.56407              | -14.63489      | -15.56407     | -15.56407     | -15.55946     | -15.56407     | -15.55946     | -15.55946     |
| $\Delta E'_{(w, m)}$ (eV) | 0         | -1.65376      | -1.85836       | 0                      | 0                      | 0              | 0             | 0             | 0             | 0             | 0             | 0             |
| $E'_{(w, m)}$ (eV)        | -13.6181  | -12.98113     | -12.77653      | -15.56407              | -15.56407              | -14.63489      | -15.56407     | -15.56407     | -15.55946     | -15.56407     | -15.55946     | -15.55946     |
| $E'_{(w, m)}$ (eV)        | -31.63247 | -31.63544     | -31.63529      | -67.69451              | -49.66493              | -31.63533      | -31.63537     | -31.63537     | -31.63535     | -31.63537     | -31.63535     | -31.63535     |
| $E'_{(w, m)}$ (eV)        | 0         | -1.65376      | -1.85836       | 0                      | 0                      | 0              | -1.85836      | -1.85836      | -1.44915      | -1.85836      | -1.44915      | -1.44915      |
| $E'_{(w, m)}$ (eV)        | -31.63537 | -33.28912     | -33.49373      | -67.69450              | -49.66493              | -31.63537      | -33.49373     | -33.49373     | -33.08452     | -33.49373     | -33.08452     | -33.08452     |
| $\omega$ ( $10^6$ rad/s)  | 44.1776   | 22.3978       | 12.2831        | 24.9286                | 24.2751                | 24.1759        | 6.21159       | 6.21159       | 10.19220      | 6.21159       | 6.29021       | 6.29021       |
| $E'_k$ (eV)               | 29.07844  | 14.74264      | 8.08494        | 16.40846               | 15.97831               | 15.91299       | 6.21159       | 6.21159       | 10.19220      | 6.21159       | 6.29021       | 6.29021       |
| $E'_{k1}$ (eV)            | -0.33749  | -0.25287      | -0.18841       | -0.25352               | -0.25017               | -0.24966       | -0.16515      | -0.16515      | -0.20896      | -0.16515      | -0.16416      | -0.16416      |
| $E'_{k2}$ (eV)            | 0.46311   | 0.12808       | 0.13328        | 0.35532                | 0.35532                | 0.35532        | 0.12312       | 0.17978       | 0.09944       | 0.12312       | 0.12312       | 0.12312       |
| $E'_{k3}$ (eV)            | [17-18]   | [19]          | [20]           | (Eq. (13.458))         | (Eq. (13.458))         | (Eq. (13.458)) | [21]          | [4]           | [5]           | [21]          | [2]           | [2]           |
| $E'_{k4}$ (eV)            | -0.10594  | -0.18883      | -0.12177       | -0.22757               | -0.14502               | -0.07200       | -0.10359      | -0.07526      | -0.15924      | -0.10359      | -0.10260      | -0.10260      |
| $E'_{k5}$ (eV)            | 0.11441   | 0.14803       | 0.14803        | 0.14803                | 0.14803                | 0.14803        | 0.14803       | 0.14803       | 0.14803       | 0.14803       | 0.14803       | 0.14803       |
| $E'_{k6}$ (eV)            | -31.74130 | -33.47795     | -33.61550      | -67.92207              | -49.80996              | -31.70737      | -33.59732     | -33.49373     | -33.24376     | -33.59732     | -33.18712     | -33.18712     |
| $E'_{k7}$ (eV)            | -13.6181  | -14.63489     | -14.63489      | -14.63489              | -14.63489              | -14.63489      | -14.63489     | -14.63489     | -14.63489     | -14.63489     | -14.63489     | -14.63489     |
| $E'_{k8}$ (eV)            | -13.59844 | 0             | 0              | -13.59844              | -13.59844              | -13.59844      | 0             | 0             | 0             | 0             | 0             | 0             |
| $E'_{k9}$ (eV)            | 4.41035   | 4.20817       | 4.34572        | 12.49186               | 7.83016                | 3.32601        | 4.32754       | 4.29921       | 3.97398       | 4.17951       | 3.62128       | 3.91734       |



Table 15.61. The total bond energies of alkyl alcohols calculated using the functional group composition and the energies of Table 15.60 compared to the experimental values [3].

| Formula                           | Name                  | OH Group | C-O (i) Group | C-O (ii) Group | CH <sub>3</sub> | CH <sub>2</sub> | CH | C-C (a) | C-C (b) | C-C (c) | C-C (d) | C-C (e) | C-C (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|-----------------------------------|-----------------------|----------|---------------|----------------|-----------------|-----------------|----|---------|---------|---------|---------|---------|---------|-----------------------------------|-------------------------------------|----------------|
| CH <sub>4</sub> O                 | Methanol              | 1        | 0             | 1              | 1               | 0               | 0  | 0       | 0       | 0       | 0       | 0       | 0       | 21.11038                          | 21.131                              | 0.00097        |
| C <sub>2</sub> H <sub>6</sub> O   | Ethanol               | 1        | 0             | 1              | 1               | 1               | 0  | 1       | 0       | 0       | 0       | 0       | 0       | 33.40563                          | 33.428                              | 0.00066        |
| C <sub>3</sub> H <sub>8</sub> O   | 1-Propanol            | 1        | 0             | 1              | 1               | 2               | 0  | 2       | 0       | 0       | 0       | 0       | 0       | 45.56333                          | 45.584                              | 0.00046        |
| C <sub>3</sub> H <sub>8</sub> O   | 2-Propanol            | 1        | 0             | 1              | 2               | 0               | 1  | 2       | 0       | 0       | 0       | 0       | 0       | 45.72088                          | 45.766                              | 0.00098        |
| C <sub>4</sub> H <sub>10</sub> O  | 1-Butanol             | 1        | 0             | 1              | 1               | 3               | 0  | 3       | 0       | 0       | 0       | 0       | 0       | 57.72103                          | 57.736                              | 0.00026        |
| C <sub>4</sub> H <sub>10</sub> O  | 2-Butanol             | 1        | 0             | 1              | 2               | 1               | 1  | 3       | 0       | 0       | 0       | 0       | 0       | 57.87858                          | 57.922                              | 0.00074        |
| C <sub>4</sub> H <sub>10</sub> O  | 2-Methyl-1-propananol | 1        | 0             | 1              | 2               | 1               | 1  | 0       | 3       | 0       | 0       | 0       | 0       | 57.79359                          | 57.828                              | 0.00060        |
| C <sub>4</sub> H <sub>10</sub> O  | 2-Methyl-2-propananol | 1        | 0             | 1              | 3               | 0               | 0  | 0       | 3       | 0       | 0       | 0       | 0       | 58.15359                          | 58.126                              | -0.00048       |
| C <sub>5</sub> H <sub>12</sub> O  | 1-Pentanol            | 1        | 0             | 1              | 1               | 4               | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 69.87873                          | 69.887                              | 0.00011        |
| C <sub>5</sub> H <sub>12</sub> O  | 2-Pentanol            | 1        | 0             | 1              | 2               | 2               | 1  | 4       | 0       | 0       | 0       | 0       | 0       | 70.03628                          | 70.057                              | 0.00029        |
| C <sub>5</sub> H <sub>12</sub> O  | 3-Pentanol            | 1        | 0             | 1              | 2               | 2               | 1  | 4       | 0       | 0       | 0       | 0       | 0       | 70.03628                          | 70.097                              | 0.00087        |
| C <sub>6</sub> H <sub>14</sub> O  | 2-Methyl-1-butanol    | 1        | 0             | 1              | 2               | 2               | 1  | 2       | 3       | 0       | 0       | 0       | 0       | 69.95129                          | 69.957                              | 0.00008        |
| C <sub>6</sub> H <sub>14</sub> O  | 3-Methyl-1-butanol    | 1        | 0             | 1              | 2               | 2               | 1  | 1       | 3       | 0       | 0       | 0       | 0       | 69.95129                          | 69.950                              | -0.00002       |
| C <sub>6</sub> H <sub>14</sub> O  | 2-Methyl-2-butanol    | 1        | 0             | 1              | 3               | 1               | 0  | 1       | 3       | 0       | 0       | 0       | 0       | 70.31129                          | 70.246                              | -0.00092       |
| C <sub>6</sub> H <sub>14</sub> O  | 3-Methyl-2-butanol    | 1        | 0             | 1              | 3               | 0               | 2  | 0       | 3       | 0       | 1       | 0       | 0       | 69.96081                          | 70.083                              | 0.00174        |
| C <sub>6</sub> H <sub>14</sub> O  | 1-Hexanol             | 1        | 0             | 1              | 1               | 5               | 0  | 5       | 0       | 0       | 0       | 0       | 0       | 82.03643                          | 82.054                              | 0.00021        |
| C <sub>6</sub> H <sub>14</sub> O  | 2-Hexanol             | 1        | 0             | 1              | 2               | 3               | 1  | 5       | 0       | 0       | 0       | 0       | 0       | 82.19398                          | 82.236                              | 0.00052        |
| C <sub>7</sub> H <sub>16</sub> O  | 1-Heptanol            | 1        | 0             | 1              | 1               | 6               | 0  | 6       | 0       | 0       | 0       | 0       | 0       | 94.19413                          | 94.214                              | 0.00021        |
| C <sub>8</sub> H <sub>18</sub> O  | 1-Octanol             | 1        | 0             | 1              | 1               | 7               | 0  | 7       | 0       | 0       | 0       | 0       | 0       | 106.35183                         | 106.358                             | 0.00006        |
| C <sub>8</sub> H <sub>18</sub> O  | 2-Ethyl-1-hexanol     | 1        | 0             | 1              | 2               | 13              | 1  | 4       | 3       | 0       | 0       | 0       | 0       | 106.42439                         | 106.459                             | 0.00032        |
| C <sub>9</sub> H <sub>20</sub> O  | 1-Nonanol             | 1        | 0             | 1              | 1               | 8               | 0  | 8       | 0       | 0       | 0       | 0       | 0       | 118.50953                         | 118.521                             | 0.00010        |
| C <sub>10</sub> H <sub>22</sub> O | 1-Decanol             | 1        | 0             | 1              | 1               | 9               | 0  | 9       | 0       | 0       | 0       | 0       | 0       | 130.66723                         | 130.676                             | 0.00007        |
| C <sub>12</sub> H <sub>26</sub> O | 1-Dodecanol           | 1        | 0             | 1              | 1               | 11              | 0  | 11      | 0       | 0       | 0       | 0       | 0       | 154.98263                         | 154.984                             | 0.00001        |
| C <sub>16</sub> H <sub>34</sub> O | 1-Hexadecanol         | 1        | 0             | 1              | 1               | 15              | 0  | 15      | 0       | 0       | 0       | 0       | 0       | 203.61343                         | 203.603                             | -0.00005       |



ETHERS ( $C_nH_{2n+2}O_m$ ,  $n=2,3,4,5\ldots\infty$ )

The alkyl ethers,  $C_nH_{2n+2}O_m$ , comprise two types of  $C-O$  functional groups, one for methyl or t-butyl groups corresponding to the  $C$  and the other for general alkyl groups. The alkyl portion of the alkyl ether may comprise at least two terminal methyl groups ( $CH_3$ ) at each  
 5 end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the  
 10 isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in ethers are equivalent to those in branched-chain alkanes.

Each  $C-O$  group is solved by hybridizing the  $2s$  and  $2p$  AOs of the  $C$  atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO  
 15 and the  $O$  AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl ethers, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) and an energy of  $E(C,2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)) and the  $O$  AO has an energy of  $E(O) = -13.61806 \text{ eV}$ . To meet the equipotential condition of the union of the  $C-O$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the  
 20  $C-O$ -bond MO given by Eq. (15.113) is  $c_2(C2sp^3HO \text{ to } O) = 0.85395$ .  $E_r(atom - atom, msp^3.AO)$  of the  $C-O$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $O$  atoms to the MO is  $-1.44915 \text{ eV}$  for the  $CH_3-O-$  and  $(CH_3)_3C-O-$   $C-O$  groups. It is based on the energy match between the  $O$  AO, initially at the Coulomb potential of a proton and an electron (Eqs. (1.236) and (10.162), respectively), and the  $C2sp^3$   
 25 HO of a methyl group as given by Eq. (14.151). For the alkyl  $C-O$  group,  $E_r(atom - atom, msp^3.AO)$  is  $-1.65376 \text{ eV}$ . It is based on the energy match between the  $O$  AO and the  $C2sp^3$  HO of a methylene group and is given by the linear combination of  $-0.72457 \text{ eV}$  (Eq. (14.151)) and  $-0.92918 \text{ eV}$  (Eq. (14.513)), respectively.

The symbols of the functional groups of branched-chain alkyl ethers are given in Table 15.63. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl ethers are given in Tables 15.64, 15.65, and 15.66, respectively. The total energy of each alkyl ether given in Table 15.67  
5 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.66 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl ethers determined using Eqs. (15.79-15.108) are given in Table 15.68.

Table 15.63. The symbols of functional groups of alkyl ethers.

| Functional Group                                           | Group Symbol          |
|------------------------------------------------------------|-----------------------|
| C-O ( $\text{CH}_3$ -O- and $(\text{CH}_3)_3\text{C-O-}$ ) | C-O (i)               |
| C-O (alkyl)                                                | C-O (ii)              |
| $\text{CH}_3$ group                                        | C-H ( $\text{CH}_3$ ) |
| $\text{CH}_2$ group                                        | C-H ( $\text{CH}_2$ ) |
| CH                                                         | C-H                   |
| CC bond (n-C)                                              | C-C (a)               |
| CC bond (iso-C)                                            | C-C (b)               |
| CC bond (tert-C)                                           | C-C (c)               |
| CC (iso to iso-C)                                          | C-C (d)               |
| CC (t to t-C)                                              | C-C (e)               |
| CC (t to iso-C)                                            | C-C (f)               |

Table 15.64. The geometrical bond parameters of alkyl ethers and experimental values [1].

| Parameter                             | C-O (i)<br>Group          | C-O (ii)<br>Group                    | C-H ( $\text{CH}_3$ )<br>Group                  | C-H ( $\text{CH}_2$ )<br>Group                  | C-H<br>Group         | C-C (a)<br>Group                        | C-C (b)<br>Group                        | C-C (c)<br>Group                        | C-C (d)<br>Group                        | C-C (e)<br>Group                        | C-C (f)<br>Group                        |
|---------------------------------------|---------------------------|--------------------------------------|-------------------------------------------------|-------------------------------------------------|----------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|
| $a$ ( $a_0$ )                         | 1.80717                   | 1.79473                              | 1.64920                                         | 1.67122                                         | 1.67465              | 2.12499                                 | 2.12499                                 | 2.10725                                 | 2.12499                                 | 2.10725                                 | 2.10725                                 |
| $c'$ ( $a_0$ )                        | 1.34431                   | 1.33968                              | 1.04856                                         | 1.05553                                         | 1.05661              | 1.45744                                 | 1.45744                                 | 1.45164                                 | 1.45744                                 | 1.45164                                 | 1.45164                                 |
| Bond Length<br>$2c'$ ( $\text{\AA}$ ) | 1.42276                   | 1.41785                              | 1.10974                                         | 1.11713                                         | 1.11827              | 1.54280                                 | 1.54280                                 | 1.53635                                 | 1.54280                                 | 1.53635                                 | 1.53635                                 |
| Exp. Bond Length<br>( $\text{\AA}$ )  | 1.416<br>(dimethyl ether) | 1.418<br>(ethyl methyl ether (avg.)) | 1.107<br>(C-H propane)<br>1.117<br>(C-H butane) | 1.107<br>(C-H propane)<br>1.117<br>(C-H butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $b, c$ ( $a_0$ )                      | 1.20776                   | 1.19429                              | 1.27295                                         | 1.29569                                         | 1.29924              | 1.54616                                 | 1.54616                                 | 1.52750                                 | 1.54616                                 | 1.52750                                 | 1.52750                                 |
| $e$                                   | 0.74388                   | 0.74645                              | 0.63580                                         | 0.63159                                         | 0.63095              | 0.68600                                 | 0.68600                                 | 0.68888                                 | 0.68600                                 | 0.68888                                 | 0.68888                                 |



Table 15.66. The energy parameters (eV) of functional groups of alkyl ethers.

| Parameters                        | C-O (i)<br>Group | C-O (ii)<br>Group | H <sub>2</sub><br>Group | H <sub>2</sub><br>Group | C-H<br>Group | C-C (a)<br>Group | C-C (b)<br>Group | C-C (c)<br>Group | C-C (d)<br>Group | C-C (e)<br>Group | C-C (f)<br>Group |
|-----------------------------------|------------------|-------------------|-------------------------|-------------------------|--------------|------------------|------------------|------------------|------------------|------------------|------------------|
| $\eta_1$                          | 1                | 1                 | 3                       | 2                       | 1            | 1                | 1                | 1                | 1                | 1                | 1                |
| $\eta_2$                          | 0                | 0                 | 2                       | 1                       | 0            | 0                | 0                | 0                | 0                | 0                | 0                |
| $\eta_3$                          | 0                | 0                 | 0                       | 0                       | 0            | 0                | 0                | 0                | 0                | 0                | 0                |
| $\zeta_1$                         | 0.5              | 0.5               | 0.75                    | 0.75                    | 0.75         | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              |
| $\zeta_2$                         | 1                | 1                 | 1                       | 1                       | 1            | 1                | 1                | 1                | 1                | 1                | 1                |
| $\zeta_3$                         | 1                | 1                 | 1                       | 1                       | 1            | 1                | 1                | 1                | 1                | 1                | 1                |
| $\zeta_4$                         | 0.85395          | 0.85395           | 0.91771                 | 0.91771                 | 0.91771      | 0.91771          | 0.91771          | 0.91771          | 0.91771          | 0.91771          | 0.91771          |
| $\zeta_5$                         | 0                | 0                 | 0                       | 1                       | 1            | 0                | 0                | 0                | 1                | 1                | 0                |
| $\zeta_6$                         | 2                | 2                 | 1                       | 1                       | 1            | 2                | 2                | 2                | 2                | 2                | 2                |
| $\zeta_7$                         | 0                | 0                 | 3                       | 2                       | 1            | 0                | 0                | 0                | 0                | 0                | 0                |
| $\zeta_8$                         | 0.5              | 0.5               | 0.75                    | 0.75                    | 0.75         | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              |
| $\zeta_9$                         | 1                | 1                 | 1                       | 1                       | 1            | 1                | 1                | 1                | 1                | 1                | 1                |
| $\zeta_{10}$                      | -33.15757        | -33.47304         | -107.32728              | -70.41425               | -35.12015    | -28.79214        | -28.79214        | -29.10112        | -28.79214        | -29.10112        | -29.10112        |
| $V_c$ (eV)                        | 10.12105         | 10.15605          | 38.92728                | 25.78002                | 12.87680     | 9.33552          | 9.33552          | 9.37273          | 9.33552          | 9.37273          | 9.37273          |
| $V_r$ (eV)                        | 9.17389          | 9.32537           | 32.33914                | 21.06675                | 10.48582     | 6.77464          | 6.77464          | 6.90500          | 6.77464          | 6.90500          | 6.90500          |
| $V_n$ (eV)                        | -4.58695         | -4.66268          | -16.26957               | -10.53537               | -5.24291     | -3.38732         | -3.38732         | -3.45250         | -3.38732         | -3.45250         | -3.45250         |
| $E_{1,0}$ (eV)                    | -14.63489        | -14.63489         | -15.56407               | -15.56407               | -14.63489    | -15.56407        | -15.56407        | -15.35946        | -15.56407        | -15.35946        | -15.35946        |
| $\Delta E_{1,0}$ (eV)             | -1.44915         | -1.65376          | 0                       | 0                       | 0            | 0                | 0                | 0                | 0                | 0                | 0                |
| $E_{1,0}^{(a)}$ (eV)              | -13.18574        | -12.98113         | -15.56407               | -15.56407               | -14.63489    | -15.56407        | -15.56407        | -15.35946        | -15.56407        | -15.35946        | -15.35946        |
| $E_{1,0}^{(b)}$ (eV)              | -31.63553        | -31.63544         | -67.69451               | -49.66493               | -31.63553    | -31.63553        | -31.63553        | -31.63553        | -31.63553        | -31.63553        | -31.63553        |
| $E_{1,0}^{(c)}$ (eV)              | -1.44915         | -1.65376          | 0                       | 0                       | 0            | -1.85836         | -1.85836         | -1.44915         | -1.85836         | -1.44915         | -1.44915         |
| $E_{1,0}^{(d)}$ (eV)              | -33.08452        | -33.28912         | -67.69450               | -49.66493               | -31.63553    | -33.49573        | -33.49573        | -33.08452        | -33.49573        | -33.08452        | -33.08452        |
| $\omega$ (10 <sup>15</sup> rad/s) | 12.0329          | 12.1583           | 24.9286                 | 24.2751                 | 24.1759      | 9.43699          | 9.43699          | 15.4846          | 9.43699          | 9.55643          | 9.55643          |
| $E_{1,0}^{(e)}$ (eV)              | 7.92028          | 8.00277           | 16.40846                | 15.97831                | 15.91299     | 6.21159          | 6.21159          | 10.19220         | 6.21159          | 6.29021          | 6.29021          |
| $E_{1,0}^{(f)}$ (eV)              | -0.18420         | -0.18631          | -0.25552                | -0.25017                | -0.24966     | -0.16515         | -0.16515         | -0.20896         | -0.16515         | -0.16416         | -0.16416         |
| $E_{1,0}^{(g)}$ (eV)              | 0.13663          | 0.16118           | 0.35532                 | 0.35532                 | 0.35532      | 0.12312          | 0.12312          | 0.09944          | 0.12312          | 0.12312          | 0.12312          |
| $E_{1,0}^{(h)}$ (eV)              | -0.11589         | -0.10572          | -0.22757                | -0.14502                | -0.07200     | -0.10359         | -0.07526         | -0.15924         | -0.10359         | -0.10260         | -0.10260         |
| $E_{1,0}^{(i)}$ (eV)              | 0.14803          | 0.14803           | 0.14803                 | 0.14803                 | 0.14803      | 0.14803          | 0.14803          | 0.14803          | 0.14803          | 0.14803          | 0.14803          |
| $E_{1,0}^{(j)}$ (eV)              | -33.20040        | -33.39484         | -67.92207               | -49.80996               | -31.70757    | -33.59732        | -33.59732        | -33.24576        | -33.59732        | -33.18712        | -33.18712        |
| $E_{1,0}^{(k)}$ (eV)              | -14.63489        | -14.63489         | -14.63489               | -14.63489               | -14.63489    | -14.63489        | -14.63489        | -14.63489        | -14.63489        | -14.63489        | -14.63489        |
| $E_{1,0}^{(l)}$ (eV)              | 0                | 0                 | -13.59844               | -13.59844               | -13.59844    | 0                | 0                | 0                | 0                | 0                | 0                |
| $E_{1,0}^{(m)}$ (eV)              | 3.93062          | 4.12506           | 12.49186                | 7.83016                 | 3.32601      | 4.32754          | 4.29921          | 3.97398          | 4.17951          | 3.62128          | 3.91734          |

Table 15.67. The total bond energies of alkyl ethers calculated using the functional group composition and the energies of Table 15.66 compared to the experimental values [3].

| Formula         | Name                    | Group | $C-O$ (i) | Group | $C-H$ | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|-----------------|-------------------------|-------|-----------|-------|-------|-----------|-----------|-----------|-----------|-----------|-----------|-----------------------------------|-------------------------------------|----------------|
| $C_2H_6O$       | Dimethyl ether          | 2     | 0         | 2     | 0     | 0         | 0         | 0         | 0         | 0         | 0         | 32.8496                           | 32.902                              | 0.00174        |
| $C_3H_8O$       | Ethyl methyl ether      | 1     | 1         | 2     | 0     | 1         | 0         | 0         | 0         | 0         | 0         | 45.19710                          | 45.183                              | -0.00030       |
| $C_4H_{10}O$    | Diethyl ether           | 0     | 2         | 2     | 0     | 2         | 0         | 0         | 0         | 0         | 0         | 57.54924                          | 57.500                              | -0.00086       |
| $C_5H_{12}O$    | Methyl propyl ether     | 1     | 1         | 2     | 0     | 2         | 0         | 0         | 0         | 0         | 0         | 57.35480                          | 57.355                              | 0.00000        |
| $C_6H_{14}O$    | Isopropyl methyl ether  | 0     | 2         | 3     | 0     | 0         | 2         | 0         | 0         | 0         | 0         | 57.45569                          | 57.499                              | 0.00075        |
| $C_6H_{14}O$    | Diisopropyl ether       | 0     | 2         | 2     | 0     | 4         | 0         | 0         | 0         | 0         | 0         | 81.86464                          | 81.817                              | -0.00059       |
| $C_7H_{16}O$    | Disopropyl ether        | 0     | 2         | 4     | 0     | 0         | 4         | 0         | 0         | 0         | 0         | 82.06642                          | 82.088                              | 0.00026        |
| $C_8H_{18}O$    | t-Butyl ethyl ether     | 1     | 1         | 4     | 1     | 0         | 1         | 0         | 0         | 0         | 0         | 82.10276                          | 82.033                              | -0.00085       |
| $C_8H_{18}O$    | t-Butyl isopropyl ether | 1     | 1         | 5     | 0     | 1         | 0         | 3         | 0         | 0         | 0         | 94.36135                          | 94.438                              | 0.00081        |
| $C_8H_{18}O$    | Dibutyl ether           | 0     | 2         | 2     | 0     | 6         | 0         | 0         | 0         | 0         | 0         | 106.18004                         | 106.122                             | -0.00055       |
| $C_9H_{20}O$    | Di-sec-butyl ether      | 0     | 2         | 4     | 2     | 2         | 0         | 0         | 0         | 0         | 0         | 106.38182                         | 106.410                             | 0.00027        |
| $C_9H_{20}O$    | Di-tert-butyl ether     | 2     | 0         | 6     | 0     | 0         | 0         | 6         | 0         | 0         | 0         | 106.55628                         | 106.425                             | -0.00218       |
| $C_{10}H_{22}O$ | t-Butyl isobutyl ether  | 1     | 1         | 5     | 1     | 0         | 3         | 0         | 0         | 0         | 0         | 106.49072                         | 106.497                             | 0.00005        |

Table 15.68. The bond angle parameters of alkyl ethers and experimental values [1]. In the calculation of  $\theta_p$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{mwp}, A(\theta))$ .

| Atom of Angle                                            | $2c'$ Bond 1 ( $a_1$ ) | $2c'$ Bond 2 ( $a_2$ ) | $2c'$ Terminal Atom ( $a_3$ ) | $I_{\text{calc}}$ Atom 1 | $I_{\text{calc}}$ Atom 2 | Hybridization Designation (Table 15.3.A) | $C_2$ Atom 1 | $C_2$ Atom 2          | $C_1$ | $C_2$ | $C_1$ | $C_2$   | $E_T$ (eV) | $\theta_p$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | Cal. $\theta$ (°) | Exp. $\theta$ (°)                                      |
|----------------------------------------------------------|------------------------|------------------------|-------------------------------|--------------------------|--------------------------|------------------------------------------|--------------|-----------------------|-------|-------|-------|---------|------------|----------------|----------------|----------------|-------------------|--------------------------------------------------------|
| $\angle C'_1 O C'_2$<br>( $C'_1 - O - C'_2$ ) (i)        | 2.68602                | 2.68602                | 4.4721                        | -17.40869                | -17.40869                | 38                                       | 0.78155      | 0.78155               | 1     | 1     | 1     | 0.78155 | -1.85836   |                |                |                | 112.54            | 112 (dimethyl ether)                                   |
| $\angle C'_1 O C'_2$<br>( $C'_1 - O - C'_2$ ) (ii)       | 2.68602                | 2.67935                | 4.4385                        | -17.31099                | -17.31099                | 41                                       | 0.77699      | 0.77699               | 1     | 1     | 1     | 0.77699 | -1.85836   |                |                |                | 111.55            | 111.9 (ethyl methyl ether)                             |
| $\angle C'_1 C'_2 C'_3$<br>( $C'_1 - C'_2 - C'_3$ ) (i)  | 2.91547                | 2.67935                | 4.5607                        | -16.68412                | -15.61806                | 0                                        | 0.81549      | 0.83595 (Eq. 15.11.4) | 1     | 1     | 1     | 0.83472 | -1.65376   |                |                |                | 109.13            | 109.4 (ethyl methyl ether)                             |
| $\angle C'_1 C'_2 C'_3$<br>( $C'_1 - C'_2 - C'_3$ ) (ii) | 2.11106                | 2.11106                | 3.4252                        | -15.75493                | -15.75493                | 7                                        | 0.86559      | 1                     | 1     | 1     | 0.75  | 1.15796 | 0          |                |                |                | 108.44            | 107 (propane)                                          |
| $\angle C'_1 C'_2 C'_3$                                  |                        |                        |                               |                          |                          |                                          |              |                       |       |       |       |         |            | 69.51          |                |                | 110.49            | 115.8 (propane)<br>110.8 (butane)<br>110.8 (isobutane) |
| $\angle C'_1 C'_2 H$                                     |                        |                        |                               |                          |                          |                                          |              |                       |       |       |       |         |            | 69.51          |                |                | 110.49            | 111.0 (butane)<br>111.4 (isobutane)                    |
| Methyl $\angle C'_1 C'_2 H$                              | 2.09711                | 2.09711                | 3.4252                        | -15.75493                | -15.75493                | 7                                        | 0.86559      | 1                     | 1     | 1     | 0.75  | 1.15796 | 0          |                |                |                | 109.50            |                                                        |
| $\angle C'_1 C'_2 C'_3$                                  |                        |                        |                               |                          |                          |                                          |              |                       |       |       |       |         |            | 70.56          |                |                | 109.44            |                                                        |
| $\angle C'_1 C'_2 C'_3$                                  |                        |                        |                               |                          |                          |                                          |              |                       |       |       |       |         |            | 70.56          |                |                | 109.44            |                                                        |
| $\angle C'_1 C'_2 C'_3$<br>iso $C'_3$                    | 2.91547                | 2.91547                | 4.7958                        | -16.68412                | -16.68412                | 25                                       | 0.81549      | 0.81549               | 1     | 1     | 1     | 0.81549 | -1.85836   |                |                |                | 110.67            | 110.8 (isobutane)                                      |
| $\angle C'_1 C'_2 H$                                     | 2.91547                | 2.11323                | 4.1633                        | -15.50033                | -14.82575                | 5                                        | 0.87495      | 0.91771               | 0.75  | 1     | 0.75  | 1.04887 | 0          |                |                |                | 110.76            |                                                        |
| $\angle C'_1 C'_2 H$                                     | 2.91547                | 2.09711                | 4.1633                        | -15.50033                | -14.82575                | 5                                        | 0.87495      | 0.91771               | 0.75  | 1     | 0.75  | 1.04887 | 0          |                |                |                | 111.27            | 111.4 (isobutane)                                      |
| $\angle C'_1 C'_2 C'_3$<br>iso $C'_3$                    | 2.90327                | 2.90327                | 4.7958                        | -15.50033                | -14.82575                | 5                                        | 0.87495      | 0.91771               | 0.75  | 1     | 0.75  | 1.04887 | -1.85836   |                |                |                | 111.27            | 111.4 (isobutane)                                      |
| $\angle C'_1 C'_2 C'_3$                                  |                        |                        |                               |                          |                          |                                          |              |                       |       |       |       |         |            | 72.50          |                |                | 107.50            |                                                        |



PRIMARY AMINES ( $C_n H_{2n+2+m} N_m$ ,  $n=1,2,3,4,5\ldots\infty$ )

The primary amines,  $C_n H_{2n+2+m} N_m$ , comprise an  $NH_2$  functional group and a  $C-N$  functional group. The alkyl portion of the primary amine may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and  
 5 methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2 CH$ ) and t-butyl  
 10 ( $(CH_3)_3 C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in primary amines are equivalent to those in branched-chain alkanes.

The primary amino ( $NH_2$ ) functional group was solved using the procedure given in the Dihydrogen Nitride ( $NH_2$ ) section. Using the results of Eqs. (13.245-13.368), the primary amino parameters in Eq. (15.52) are  $n_1 = 2$ ,  $C_1 = 0.75$ ,  $C_2 = 0.93613$  (Eqs. (13.248-13.249)),  
 15  $C_{10} = 1.5$ , and  $c_1 = 0.75$ . In primary amines, the  $C2sp^3$  HO of the  $C-NH_2$ -bond MO has an energy of  $E(C, 2sp^3) = -15.35946 \text{ eV}$  (Eq. (15.18) with  $s=1$  and Eqs. (15.19-15.20)) and the  $N$  AO has an energy of  $E(N) = -14.53414 \text{ eV}$ . To meet the equipotential condition of the union of the  $N-H$   $H_2$ -type-ellipsoidal-MO with the  $C2sp^3$  HO, the hybridization factor  $c_2$  of Eq. (15.52) for the  $N-H$ -bond MO given by Eq. (15.68) is

$$20 \quad c_2(H \text{ to } 1^\circ N) = \frac{E(N)}{E(C, 2sp^3)} = \frac{-14.53414 \text{ eV}}{-15.35946 \text{ eV}} = 0.94627 \quad (15.115)$$

The  $C-N$  group is solved by hybridizing the  $2s$  and  $2p$  AOs of the  $C$  atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the  $N$  AO to form a MO permits each participating orbital to decrease in radius and energy. In primary amines, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a  
 25 corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)), and the  $N$  AO has an energy of  $E(N) = -14.53414 \text{ eV}$ . To meet the equipotential condition of the union of the

$C-N$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the  $C-N$ -bond MO given by Eqs. (15.68) and (15.70) is

$$c_2(C2sp^3HO \text{ to } N) = \frac{E(N)}{E(C, 2sp^3)} c_2(C2sp^3HO) = \frac{-14.53414 \text{ eV}}{-14.63489 \text{ eV}} (0.91771) = 0.91140 \quad (15.116)$$

$E_T(\text{atom-atom}, msp^3.AO)$  of the  $C-N$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $N$  atoms to the MO is  $-1.44915 \text{ eV}$ . It is based on the energy match between the  $N$  of the  $NH_2$  group and the  $C2sp^3$  HO corresponding to the energy contributions to the single bond that are equivalent to those of methyl groups,  $-0.72457 \text{ eV}$  (Eq. (14.151)), where the  $N-H$  bonds are also energy matched to the  $C-N$  bond.

The symbols of the functional groups of branched-chain primary amines are given in Table 15.69. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of primary amines are given in Tables 15.70, 15.71, and 15.72, respectively. The total energy of each primary amine given in Table 15.73 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.72 corresponding to functional-group composition of the molecule. The bond angle parameters of primary amines determined using Eqs. (15.79-15.108) are given in Table 15.74.

Table 15.69. The symbols of functional groups of primary amines.

| Functional Group  | Group Symbol |
|-------------------|--------------|
| $NH_2$ group      | $NH_2$       |
| C-N               | $C-N$        |
| $CH_3$ group      | $C-H (CH_3)$ |
| $CH_2$ group      | $C-H (CH_2)$ |
| CH                | $C-H$        |
| CC bond (n-C)     | $C-C$ (a)    |
| CC bond (iso-C)   | $C-C$ (b)    |
| CC bond (tert-C)  | $C-C$ (c)    |
| CC (iso to iso-C) | $C-C$ (d)    |
| CC (t to t-C)     | $C-C$ (e)    |
| CC (t to iso-C)   | $C-C$ (f)    |

Table 15.70. The geometrical bond parameters of primary amines and experimental values [1].

| Parameter                                | $NH_2$<br>Group        | $C-N$<br>Group         | $C-H$<br>Group                                        | $C-H$<br>Group       | $C-C$<br>Group       | $C-C$<br>Group                          | $C-C$<br>Group                          | $C-C$<br>Group                          | $C-C$<br>Group                          |
|------------------------------------------|------------------------|------------------------|-------------------------------------------------------|----------------------|----------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|
| $a$ ( $a_0$ )                            | 1.28083                | 1.92682                | 1.64920                                               | 1.67122              | 1.67465              | 2.12499                                 | 2.12499                                 | 2.10725                                 | 2.10725                                 |
| $c'$ ( $a_0$ )                           | 0.95506                | 1.38810                | 1.04856                                               | 1.05553              | 1.05661              | 1.45744                                 | 1.45744                                 | 1.45164                                 | 1.45164                                 |
| Bond<br>Length<br>$2c'$ ( $\text{\AA}$ ) | 1.0108                 | 1.0974                 | 1.11713                                               | 1.11827              | 1.11827              | 1.54280                                 | 1.54280                                 | 1.53635                                 | 1.53635                                 |
| Exp. Bond<br>Length<br>( $\text{\AA}$ )  | 1.010<br>(methylamine) | 1.471<br>(methylamine) | 1.107<br>( $C-H$ propane)<br>1.117<br>( $C-H$ butane) | 1.122<br>(isobutane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $b_{1c}$ ( $a_0$ )                       | 0.85345                | 1.33634                | 1.27295                                               | 1.29569              | 1.29924              | 1.54616                                 | 1.54616                                 | 1.52750                                 | 1.52750                                 |
| $e$                                      | 0.74566                | 0.72041                | 0.63580                                               | 0.63159              | 0.63095              | 0.68600                                 | 0.68600                                 | 0.68888                                 | 0.68888                                 |

Table 15.71. The MO to HO intercept geometrical bond parameters of primary amines.  $R, R', R''$  are  $H$  or alkyl groups.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{mwp}, \text{AO})$ .

| Bond                                                           | Atom | $E_T$<br>(eV)<br>Bond 1 | $E_T$<br>(eV)<br>Bond 2 | $E_T$<br>(eV)<br>Bond 3 | $E_T$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>$C2_{sp^3}$<br>(eV) | $r_{ind}$<br>( $a_0$ ) | $r_{ind}$<br>( $a_0$ ) | $E_{C_{ind}}$<br>(eV)<br>Final | $E(C2_{sp^3})$<br>(eV)<br>Final | $\theta^*$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | $d_1$<br>( $a_0$ ) | $d_2$<br>( $a_0$ ) |
|----------------------------------------------------------------|------|-------------------------|-------------------------|-------------------------|-------------------------|----------------------------------------------|------------------------|------------------------|--------------------------------|---------------------------------|----------------------------|----------------------------|----------------------------|--------------------|--------------------|
| $H_2C(NH) - H$                                                 | N    | -0.72457                | 0                       | 0                       | 0                       | -15.50033                                    | 0.90084                | 0.87495                | -15.50033                      | 118.00                          | 118.00                     | 62.00                      | 64.85                      | 0.54432            | 0.41075            |
| $-H_2C(NH) - H$                                                | N    | -0.72457                | 0                       | 0                       | 0                       | -15.50033                                    | 0.90084                | 0.87495                | -15.50033                      | 118.00                          | 118.00                     | 62.00                      | 64.85                      | 0.54432            | 0.41075            |
| $H_2C - NH_2$                                                  | C    | -0.72457                | 0                       | 0                       | 0                       | -152.34026                                   | 0.91771                | 0.87495                | -15.50033                      | -15.35946                       | 85.28                      | 94.72                      | 40.73                      | 1.46010            | 0.07200            |
| $H_2C - NH_2$                                                  | N    | -0.72457                | 0                       | 0                       | 0                       | -15.50033                                    | 0.90084                | 0.87495                | -15.50033                      | 85.28                           | 85.28                      | 94.72                      | 40.73                      | 1.46010            | 0.07200            |
| $-H_2C - NH_2$                                                 | C    | -0.72457                | -0.92918                | 0                       | 0                       | -153.25945                                   | 0.91771                | 0.82562                | -16.47951                      | -16.28864                       | 80.20                      | 99.80                      | 37.50                      | 1.52858            | 0.14048            |
| $-H_2C - NH_2$                                                 | N    | -0.72457                | 0                       | 0                       | 0                       | -15.50033                                    | 0.90084                | 0.87495                | -15.50033                      | 85.28                           | 85.28                      | 94.72                      | 40.73                      | 1.46010            | 0.07200            |
| $C - H$ ( $CH_3$ )                                             | C    | -0.92918                | 0                       | 0                       | 0                       | -152.34487                                   | 0.91771                | 0.86359                | -15.75493                      | -15.56407                       | 77.49                      | 102.51                     | 41.48                      | 1.23564            | 0.18708            |
| $C - H$ ( $CH_3$ )                                             | C    | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                   | 0.91771                | 0.81549                | -16.68412                      | -16.49325                       | 68.47                      | 111.53                     | 35.84                      | 1.3486             | 0.29933            |
| $C - H$ ( $CH$ )                                               | C    | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                   | 0.91771                | 0.77247                | -17.61330                      | -17.42244                       | 61.10                      | 118.90                     | 31.37                      | 1.42988            | 0.37326            |
| $H_2C, C, H_2, CH_2 -$<br>( $C - C$ )                          | C    | -0.92918                | 0                       | 0                       | 0                       | -152.34487                                   | 0.91771                | 0.86359                | -15.75493                      | -15.56407                       | 63.82                      | 116.18                     | 30.08                      | 1.83879            | 0.38106            |
| $H_2C, C, H_2, CH_2 -$<br>( $C - C$ )                          | C    | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                   | 0.91771                | 0.81549                | -16.68412                      | -16.49325                       | 56.41                      | 123.59                     | 26.06                      | 1.90890            | 0.45117            |
| $R - H_2C, C, (H_2C - R)HCH_2 -$<br>( $C - C$ )                | C    | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                   | 0.91771                | 0.77247                | -17.61330                      | -17.42244                       | 48.30                      | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| $R - H_2C, C, (R' - H_2C)C, (R'' - H_2C)CH_2 -$<br>( $C - C$ ) | C    | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -154.71860                                   | 0.91771                | 0.73889                | -17.92866                      | -17.73779                       | 48.21                      | 131.79                     | 21.74                      | 1.95734            | 0.50570            |
| $R - H_2C, C, (H_2C - R)HCH_2 -$<br>( $C - C$ )                | C    | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                   | 0.91771                | 0.77247                | -17.61330                      | -17.42244                       | 48.30                      | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| $R - H_2C, C, (R' - H_2C)C, (R'' - H_2C)CH_2 -$<br>( $C - C$ ) | C    | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -154.51999                                   | 0.91771                | 0.76765                | -17.92866                      | -17.73779                       | 50.04                      | 129.96                     | 22.66                      | 1.94462            | 0.49298            |
| $R - H_2C, C, (R' - H_2C)C, (R'' - H_2C)CH_2 -$<br>( $C - C$ ) | C    | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.19863                                   | 0.91771                | 0.78155                | -17.40869                      | -17.21783                       | 52.78                      | 127.22                     | 24.04                      | 1.92443            | 0.47279            |
| $R - H_2C, C, (R' - H_2C)C, (R'' - H_2C)CH_2 -$<br>( $C - C$ ) | C    | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -154.51999                                   | 0.91771                | 0.76765                | -17.92866                      | -17.73779                       | 50.04                      | 129.96                     | 22.66                      | 1.94462            | 0.49298            |

Table 15.72. The energy parameters (eV) of functional groups of primary amines

| Parameters                        | NH <sub>2</sub><br>Group | C-N<br>Group | CH <sub>3</sub><br>Group | CH <sub>2</sub><br>Group | C-H<br>Group | C-C (a)<br>Group | C-C (b)<br>Group | C-C (c)<br>Group | C-C (d)<br>Group | C-C (e)<br>Group | C-C (f)<br>Group |
|-----------------------------------|--------------------------|--------------|--------------------------|--------------------------|--------------|------------------|------------------|------------------|------------------|------------------|------------------|
| $n_1$                             | 2                        | 1            | 3                        | 2                        | 1            | 1                | 1                | 1                | 1                | 1                | 1                |
| $n_2$                             | 0                        | 0            | 2                        | 1                        | 0            | 0                | 0                | 0                | 0                | 0                | 0                |
| $n_3$                             | 1                        | 0            | 0                        | 0                        | 0            | 0                | 0                | 0                | 0                | 0                | 0                |
| $C_1$                             | 0.75                     | 0.5          | 0.75                     | 0.75                     | 0.75         | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              |
| $C_2$                             | 0.93613                  | 1            | 1                        | 1                        | 1            | 1                | 1                | 1                | 1                | 1                | 1                |
| $C_3$                             | 0.75                     | 1            | 1                        | 1                        | 1            | 1                | 1                | 1                | 1                | 1                | 1                |
| $C_4$                             | 0.94627                  | 0.91440      | 0.91771                  | 0.91771                  | 0.91771      | 0.91771          | 0.91771          | 0.91771          | 0.91771          | 0.91771          | 0.91771          |
| $C_5$                             | 0                        | 0            | 0                        | 1                        | 1            | 0                | 0                | 0                | 1                | 1                | 0                |
| $C_6$                             | 1                        | 2            | 1                        | 1                        | 1            | 2                | 2                | 2                | 2                | 2                | 2                |
| $C_7$                             | 2                        | 0            | 3                        | 2                        | 1            | 0                | 0                | 0                | 0                | 0                | 0                |
| $C_{10}$                          | 1.5                      | 0.5          | 0.75                     | 0.75                     | 0.75         | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              |
| $C_{10}$                          | 1                        | 1            | 1                        | 1                        | 1            | 1                | 1                | 1                | 1                | 1                | 1                |
| $V_c$ (eV)                        | -77.89807                | -32.46339    | -107.32728               | -70.41425                | -35.12015    | -28.79214        | -28.79214        | -29.10112        | -28.79214        | -29.10112        | -29.10112        |
| $V_s$ (eV)                        | 28.49191                 | 9.80175      | 38.92728                 | 25.78002                 | 12.87680     | 9.33352          | 9.33352          | 9.37273          | 9.33352          | 9.37273          | 9.37273          |
| $T$ (eV)                          | 30.40957                 | 8.42409      | 32.53914                 | 21.06675                 | 10.48582     | 6.77464          | 6.77464          | 6.90500          | 6.77464          | 6.90500          | 6.90500          |
| $V_p$ (eV)                        | -15.20478                | -4.21204     | -16.26957                | -10.53337                | -5.24291     | -3.38732         | -3.38732         | -3.45250         | -3.38732         | -3.45250         | -3.45250         |
| $E_{1,100}^{(1,100)}$ (eV)        | -14.53414                | -14.63489    | -15.56407                | -15.56407                | -14.63489    | -15.56407        | -15.56407        | -15.35946        | -15.56407        | -15.35946        | -15.35946        |
| $\Delta E_{1,100}^{(1,100)}$ (eV) | 0                        | -1.44915     | 0                        | 0                        | 0            | 0                | 0                | 0                | 0                | 0                | 0                |
| $E_{1,100}^{(1,100)}$ (eV)        | -14.53414                | -13.18574    | -15.56407                | -15.56407                | -14.63489    | -15.56407        | -15.56407        | -15.35946        | -15.56407        | -15.35946        | -15.35946        |
| $E_{1,100}^{(1,100)}$ (eV)        | -14.53414                | 0            | 0                        | 0                        | 0            | 0                | 0                | 0                | 0                | 0                | 0                |
| $E_{1,100}^{(1,100)}$ (eV)        | -48.73642                | -31.63534    | -67.69451                | -49.66493                | -31.63533    | -31.63537        | -31.63537        | -31.63535        | -31.63537        | -31.63535        | -31.63535        |
| $E_{1,100}^{(1,100)}$ (eV)        | 0                        | -1.44915     | 0                        | 0                        | 0            | -1.85836         | -1.85836         | -1.44915         | -1.85836         | -1.44915         | -1.44915         |
| $E_{1,100}^{(1,100)}$ (eV)        | -48.73660                | -33.08452    | -67.69450                | -49.66493                | -31.63537    | -33.49373        | -33.49373        | -33.08452        | -33.49373        | -33.08452        | -33.08452        |
| $\omega$ (10 <sup>5</sup> rad/s)  | 64.2189                  | 18.9231      | 24.9786                  | 24.2751                  | 24.1759      | 9.43699          | 9.43699          | 15.4846          | 9.43699          | 9.55643          | 9.55643          |
| $E_{1,100}^{(1,100)}$ (eV)        | 42.27003                 | 12.45552     | 16.40846                 | 15.97831                 | 15.91299     | 6.21159          | 6.21159          | 10.19220         | 6.21159          | 6.29021          | 6.29021          |
| $E_{1,100}^{(1,100)}$ (eV)        | -0.40690                 | -0.23100     | -0.25352                 | -0.25017                 | -0.24966     | -0.16515         | -0.16515         | -0.20896         | -0.16515         | -0.16416         | -0.16416         |
| $E_{1,100}^{(1,100)}$ (eV)        | 0.40929                  | 0.12944      | 0.35532                  | 0.35532                  | 0.35532      | 0.12312          | 0.17978          | 0.09944          | 0.12312          | 0.12312          | 0.12312          |
| $E_{1,100}^{(1,100)}$ (eV)        | 122                      | 23           | Eq. (13.458)             | Eq. (13.458)             | Eq. (13.458) | 2                | 4                | 5                | 2                | 2                | 2                |
| $E_{1,100}^{(1,100)}$ (eV)        | -0.20226                 | -0.16628     | -0.22757                 | -0.14502                 | -0.07200     | -0.10359         | -0.07526         | -0.15924         | -0.10359         | -0.10260         | -0.10260         |
| $E_{1,100}^{(1,100)}$ (eV)        | 0.14803                  | 0.14803      | 0.14803                  | 0.14803                  | 0.14803      | 0.14803          | 0.14803          | 0.14803          | 0.14803          | 0.14803          | 0.14803          |
| $E_{1,100}^{(1,100)}$ (eV)        | -49.14112                | -33.25079    | -67.92207                | -49.80996                | -31.70737    | -33.59732        | -33.49373        | -33.24376        | -33.59732        | -33.18712        | -33.18712        |
| $E_{1,100}^{(1,100)}$ (eV)        | -14.53414                | -14.63489    | -14.63489                | -14.63489                | -14.63489    | -14.63489        | -14.63489        | -14.63489        | -14.63489        | -14.63489        | -14.63489        |
| $E_{1,100}^{(1,100)}$ (eV)        | -13.59844                | 0            | -13.59844                | -13.59844                | -13.59844    | 0                | 0                | 0                | 0                | 0                | 0                |
| $E_{1,100}^{(1,100)}$ (eV)        | 7.41010                  | 3.98101      | 12.49186                 | 7.83016                  | 3.32601      | 4.32754          | 4.29921          | 3.97398          | 4.17951          | 3.62128          | 3.91734          |

Table 15.73. The total bond energies of primary amines calculated using the functional group composition and the energies of Table 15.72 compared to the experimental values [3]

| Formula                         | NH <sub>2</sub><br>Group | C-N<br>Group | CH <sub>3</sub><br>Group | CH <sub>2</sub><br>Group | CH<br>Group | C-C (a)<br>Group | C-C (b)<br>Group | C-C (c)<br>Group | C-C (d)<br>Group | C-C (e)<br>Group | C-C (f)<br>Group | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|---------------------------------|--------------------------|--------------|--------------------------|--------------------------|-------------|------------------|------------------|------------------|------------------|------------------|------------------|-----------------------------------------|-------------------------------------------|----------------|
| CH <sub>3</sub> N               | 1                        | 1            | 1                        | 0                        | 0           | 0                | 0                | 0                | 0                | 0                | 0                | 23.837                                  | 23.837                                    | -0.00110       |
| C <sub>2</sub> H <sub>5</sub> N | 1                        | 1            | 1                        | 1                        | 0           | 0                | 0                | 0                | 0                | 0                | 0                | 36.0067                                 | 36.062                                    | 0.00060        |
| C <sub>3</sub> H <sub>7</sub> N | 1                        | 1            | 1                        | 2                        | 0           | 0                | 0                | 0                | 0                | 0                | 0                | 48.19837                                | 48.243                                    | 0.00092        |
| C <sub>4</sub> H <sub>9</sub> N | 1                        | 1            | 1                        | 3                        | 0           | 0                | 0                | 0                | 0                | 0                | 0                | 60.35007                                | 60.415                                    | 0.00098        |
| sec-Buylamine                   | 1                        | 1            | 2                        | 0                        | 1           | 0                | 2                | 0                | 0                | 0                | 0                | 60.45696                                | 60.547                                    | 0.00148        |
| t-Buylamine                     | 1                        | 1            | 3                        | 0                        | 0           | 0                | 0                | 3                | 0                | 0                | 0                | 60.717                                  | 60.717                                    | -0.00118       |
| Isobutylamine                   | 1                        | 1            | 2                        | 1                        | 1           | 0                | 3                | 0                | 0                | 0                | 0                | 60.42863                                | 60.486                                    | 0.00094        |

Table 15.74. The bond angle parameters of primary amines and experimental values [1]. In the calculation of  $\theta_s$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{mwp}, \text{AO})$ .

| Atom of Angle                               | $2c'$<br>Bond 1<br>( $a_0$ ) | $2c'$<br>Bond 2<br>( $a_0$ ) | $2c'$<br>Terminal<br>Atoms ( $a_0$ ) | $E_{\text{residual}}$<br>or<br>$E_T$<br>Atom 1 | Atom 1<br>Hybridization<br>Designation<br>(Table 15.3.A) | $E_{\text{residual}}$<br>or<br>$E_T$<br>Atom 2 | Atom 2<br>Hybridization<br>Designation<br>(Table 15.3.A) | $c_2$<br>Atom 1           | $c_2$<br>Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c'_1$  | $E_T$<br>(eV) | $\theta_r$<br>( $^\circ$ ) | $\theta_s$<br>( $^\circ$ ) | Cal. $\theta$<br>( $^\circ$ ) | Exp. $\theta$<br>( $^\circ$ )                                 |
|---------------------------------------------|------------------------------|------------------------------|--------------------------------------|------------------------------------------------|----------------------------------------------------------|------------------------------------------------|----------------------------------------------------------|---------------------------|-----------------|-------|-------|-------|---------|---------------|----------------------------|----------------------------|-------------------------------|---------------------------------------------------------------|
| $\angle \text{HNH}$                         | 1.91013                      | 1.91013                      | 3.0984                               | -14.53414                                      | N                                                        | H                                              | H                                                        | 0.94627<br>(Eq. (15.115)) | 1               | 1     | 1     | 0.75  | 1.05579 | 0             |                            |                            | 108.40                        | 107.1<br>(methylamine)                                        |
| $\angle \text{HNC}$                         | 1.91013                      | 2.77620                      | 3.8816                               | -14.53414                                      | S                                                        |                                                | N                                                        | 0.91140<br>(Eq. (15.116)) | 0.88583         | 0.75  | 1     | 0.75  | 0.97194 | 0             |                            |                            | 110.48                        | 110.3<br>(methylamine)                                        |
| Methyl<br>$\angle \text{HC}_\alpha\text{H}$ | 2.11106                      | 2.11106                      | 3.4252                               | -15.75493                                      | 7                                                        | H                                              | H                                                        | 0.86359                   | 1               | 1     | 1     | 0.75  | 1.15796 | 0             |                            |                            | 108.44                        | 108.0<br>(methylamine)                                        |
| $\angle \text{C}'_a\text{C}'_b\text{C}'_c$  |                              |                              |                                      |                                                |                                                          |                                                |                                                          |                           |                 |       |       |       |         |               | 69.51                      |                            |                               | 112<br>(propane)<br>113.8<br>(butane)<br>110.8<br>(isobutane) |
| $\angle \text{C}'_a\text{C}'_b\text{H}$     |                              |                              |                                      |                                                |                                                          |                                                |                                                          |                           |                 |       |       |       |         |               | 69.51                      |                            |                               | 111.0<br>(butane)<br>111.4<br>(isobutane)                     |
| Methyl<br>$\angle \text{HC}_\alpha\text{H}$ | 2.09711                      | 2.09711                      | 3.4252                               | -15.75493                                      | 7                                                        | H                                              | H                                                        | 0.86359                   | 1               | 1     | 1     | 0.75  | 1.15796 | 0             |                            |                            | 109.50                        |                                                               |
| $\angle \text{C}'_a\text{C}'_b\text{C}'_c$  |                              |                              |                                      |                                                |                                                          |                                                |                                                          |                           |                 |       |       |       |         |               |                            | 70.56                      | 109.44                        |                                                               |
| $\angle \text{C}'_a\text{C}'_b\text{H}$     |                              |                              |                                      |                                                |                                                          |                                                |                                                          |                           |                 |       |       |       |         |               |                            | 70.56                      | 109.44                        |                                                               |
| $\angle \text{C}'_a\text{C}'_b\text{C}'_c$  | 2.91547                      | 2.91547                      | 4.7958                               | -16.68412                                      | 25                                                       | $\text{C}'_c$                                  | 25                                                       | 0.81549                   | 0.81549         | 1     | 1     | 1     | 0.81549 | -1.85836      |                            |                            | 110.67                        | 110.8<br>(isobutane)                                          |
| $\angle \text{C}'_a\text{C}'_b\text{H}$     | 2.91547                      | 2.11323                      | 4.1633                               | -15.55033                                      | 5                                                        | $\text{C}'_a$                                  | 1                                                        | 0.87495                   | 0.91771         | 0.75  | 1     | 0.75  | 1.04887 | 0             |                            |                            | 110.76                        |                                                               |
| $\angle \text{C}'_a\text{C}'_b\text{H}$     | 2.91547                      | 2.09711                      | 4.1633                               | -15.55033                                      | 5                                                        | $\text{C}'_b$                                  | 1                                                        | 0.87495                   | 0.91771         | 0.75  | 1     | 0.75  | 1.04887 | 0             |                            |                            | 111.27                        | 111.4<br>(isobutane)                                          |
| $\angle \text{C}'_a\text{C}'_b\text{C}'_c$  | 2.90327                      | 2.90327                      | 4.7958                               | -15.55033                                      | 5                                                        | $\text{C}'_a$                                  | 1                                                        | 0.87495                   | 0.91771         | 0.75  | 1     | 0.75  | 1.04887 | -1.85836      |                            |                            | 111.27                        | 111.4<br>(isobutane)                                          |
| $\angle \text{C}'_a\text{C}'_b\text{C}'_d$  |                              |                              |                                      |                                                |                                                          |                                                |                                                          |                           |                 |       |       |       |         |               | 72.50                      |                            | 107.50                        |                                                               |

SECONDARY AMINES ( $C_n H_{2n+2+m} N_m$ ,  $n = 2, 3, 4, 5 \dots \infty$ )

The secondary amines,  $C_n H_{2n+2+m} N_m$ , comprise an  $NH$  functional group and two types of  $C-N$  functional groups, one for the methyl group corresponding to the  $C$  of  $C-N$  and the other for general alkyl secondary amines. The alkyl portion of the secondary amine may  
 5 comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl  
 10 ( $(CH_3)_2 CH$ ) and t-butyl ( $(CH_3)_3 C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in secondary amines are equivalent to those in branched-chain alkanes.

The secondary amino ( $NH$ ) functional group was solved using the procedure given in the Hydrogen Nitride ( $NH$ ) section. Using the results of Eqs. (13.245-13.316), the secondary  
 15 amino parameters in Eq. (15.52) are  $n_1 = 1$ ,  $C_1 = 0.75$ ,  $C_2 = 0.93613$  (Eqs. (13.248-13.249)),  $C_{1o} = 0.75$ , and  $c_1 = 0.75$ . In secondary amines, the  $C2sp^3$  HO of the  $C-NH$ -bond MO has an energy of  $E(C, 2sp^3) = -15.56407 \text{ eV}$  (Eqs. (14.514-14.516)); Eq. (15.29) with  $s = 1$  and  $s = 2$ , Eq. (15.31), and Eqs. (15.19-15.20)) and the  $N$  AO has an energy of  $E(N) = -14.53414 \text{ eV}$ . To meet the equipotential condition of the union of the  $N-H$   $H_2$ -  
 20 type-ellipsoidal-MO with the  $C2sp^3$  HO, the hybridization factor  $c_2$  of Eq. (15.52) for the  $N-H$ -bond MO given by Eq. (15.68) is

$$c_2(H \text{ to } 2^\circ N) = \frac{E(N)}{E(C, 2sp^3)} = \frac{-14.53414 \text{ eV}}{-15.56407 \text{ eV}} = 0.93383 \quad (15.117)$$

The  $C-N$  group is solved by hybridizing the  $2s$  and  $2p$  AOs of the  $C$  atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the  
 25  $N$  AO to form a MO permits each participating orbital to decrease in radius and energy. In secondary amines, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)), and the  $N$  AO has an energy of  $E(N) = -14.53414 \text{ eV}$ . To meet the equipotential condition of the union of the

$C-N$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the  $C-N$ -bond MO given by Eq. (15.116) is  $c_2(C2sp^3HO \text{ to } N) = 0.91140$ .

As given in the Continuous-Chain Alkanes ( $C_nH_{2n+2}$ ,  $n = 3, 4, 5, \dots, \infty$ ) section, each methylene group forms two single bonds, and the energy of each  $C2sp^3$  HO of each  $CH_2$  group alone is given by that in ethylene,  $-1.13379 \text{ eV}$  (Eq. (14.511)). In secondary amines, the  $N$  of the  $NH$  group also binds to two  $C2sp^3$  HOs and the corresponding  $E_T(\text{atom} - \text{atom}, msp^3.AO)$  of each  $C-N$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $N$  atoms to the MO is  $-1.13379 \text{ eV}$ . It is based on the energy match between the  $N$  of the  $NH$  group to the two  $C2sp^3$  HOs corresponding to the energy contributions to each of the two single bonds that are equivalent to those of independent methylene groups,  $-1.13379 \text{ eV}$  (Eq. (14.511)), where the  $N-H$  bond is also energy matched to the  $C-N$  bonds.  $E_T(\text{atom} - \text{atom}, msp^3.AO)$  of the  $C-N$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $N$  atoms to the MO is  $-1.13379 \text{ eV}$ . It is based on the energy match between the  $N$  of the  $NH$  group to two  $C2sp^3$  HOs corresponding to the energy contributions to the single bond that are equivalent to those of methyl groups,  $-0.72457 \text{ eV}$  (Eq. (14.151)), where the  $N-H$  bonds are also energy matched to the  $C-N$  bond.

The symbols of the functional groups of branched-chain secondary amines are given in Table 15.75. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of secondary amines are given in Tables 15.76, 15.77, and 15.78, respectively. As in the case of  $NH_2$  (Eq. (13.339)),  $C_{1o} = 2C_1$  rather than  $C_{1o} = C_1$  in Eq. (15.52) for the  $C-N$  bond. The total energy of each secondary amine given in Table 15.79 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.78 corresponding to functional-group composition of the molecule. The bond angle parameters of secondary amines determined using Eqs. (15.79-15.108) are given in Table 15.80.

Table 15.75. The symbols of functional groups of secondary amines.

| Functional Group  | Group Symbol     |
|-------------------|------------------|
| NH group          | $NH$             |
| C-N (methyl)      | $C-N$ (i)        |
| C-N (alkyl)       | $C-N$ (ii)       |
| $CH_3$ group      | $C-H$ ( $CH_3$ ) |
| $CH_2$ group      | $C-H$ ( $CH_2$ ) |
| CH                | $C-H$            |
| CC bond (n-C)     | $C-C$ (a)        |
| CC bond (iso-C)   | $C-C$ (b)        |
| CC bond (tert-C)  | $C-C$ (c)        |
| CC (iso to iso-C) | $C-C$ (d)        |
| CC (t to t-C)     | $C-C$ (e)        |
| CC (t to iso-C)   | $C-C$ (f)        |



Table 15.76. The geometrical bond parameters of secondary amines and experimental values [1].

| Parameter                  | NH Group             | C-N (f) Group         | C-N (ti) Group      | C-H (CH <sub>3</sub> ) Group | C-H (CH <sub>2</sub> ) Group | C-H Group         | C-C (a) Group   | C-C (b) Group   | C-C (c) Group   | C-C (d) Group   | C-C (e) Group   | C-C (f) Group   |
|----------------------------|----------------------|-----------------------|---------------------|------------------------------|------------------------------|-------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $\sigma$ (a <sub>0</sub> ) | 1.26224              | 1.94862               | 1.94862             | 1.64920                      | 1.67122                      | 1.67465           | 2.12499         | 2.12499         | 2.10725         | 2.12499         | 2.10725         | 2.10725         |
| $c'$ (a <sub>0</sub> )     | 0.94811              | 1.39593               | 1.39593             | 1.04856                      | 1.05553                      | 1.05661           | 1.45744         | 1.45744         | 1.45164         | 1.45744         | 1.45164         | 1.45164         |
| Bond Length 2c' (Å)        | 1.00343              | 1.47739               | 1.47739             | 1.10974                      | 1.11713                      | 1.11827           | 1.54280         | 1.54280         | 1.53635         | 1.54280         | 1.53635         | 1.53635         |
| Exp. Bond Length (Å)       | 1.00 (dimethylamine) | 1.455 (dimethylamine) | 1.107 (C-H propane) | 1.107 (C-H propane)          | 1.117 (C-H propane)          | 1.122 (isobutane) | 1.532 (propane) | 1.532 (propane) | 1.532 (propane) | 1.532 (propane) | 1.532 (propane) | 1.532 (propane) |
| $h_c$ (a <sub>0</sub> )    | 0.83327              | 1.35960               | 1.35960             | 1.27295                      | 1.29569                      | 1.29924           | 1.54616         | 1.54616         | 1.52750         | 1.54616         | 1.52750         | 1.52750         |
| $\epsilon$                 | 0.75113              | 0.71637               | 0.71637             | 0.63380                      | 0.63159                      | 0.63095           | 0.68600         | 0.68600         | 0.68888         | 0.68600         | 0.68888         | 0.68888         |

Table 15.77. The MO to HO intercept geometrical bond parameters of secondary amines.  $R, R', R''$  are H or alkyl groups.  $E_f$  is  $E_f(\text{atom} - \text{atom}, \text{misp}^3, \text{AO})$ .

| Bond                         | Atom           | $E_f$ (eV) Bond 1 | $E_f$ (eV) Bond 2 | $E_f$ (eV) Bond 3 | $E_f$ (eV) Bond 4 | Final Total Energy $C^{2sp^3}$ (eV) | $r_{\text{final}}$ (a <sub>0</sub> ) | $r_{\text{final}}$ (a <sub>0</sub> ) | $E_{\text{Final}}$ (eV) Final | $E(C^{2sp^3})$ (eV) Final | $\theta^*$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ (a <sub>0</sub> ) | $d_2$ (a <sub>0</sub> ) |
|------------------------------|----------------|-------------------|-------------------|-------------------|-------------------|-------------------------------------|--------------------------------------|--------------------------------------|-------------------------------|---------------------------|----------------|----------------|----------------|-------------------------|-------------------------|
| $H_2C-N(C_2H_5)-H$           | N              | -0.56690          | -0.56690          | 0                 | 0                 | -152.18259                          | 0.93084                              | 0.85252                              | -15.95954                     | -15.95954                 | 118.18         | 61.82          | 64.40          | 0.54546                 | 0.40264                 |
| $-H_2C-N(R_{\text{misp}})-H$ | N              | -0.56690          | -0.56690          | 0                 | 0                 | -152.18259                          | 0.93084                              | 0.85252                              | -15.95954                     | -15.95954                 | 118.18         | 61.82          | 64.40          | 0.54546                 | 0.40264                 |
| $H_2C-NH-C_2H_5$             | C <sub>u</sub> | -0.56690          | 0                 | 0                 | 0                 | -152.18259                          | 0.91771                              | 0.88392                              | -15.39265                     | -15.20178                 | 84.14          | 95.86          | 40.30          | 1.48625                 | 0.09032                 |
| $H_2C-NH-C_2H_5$             | N              | -0.56690          | -0.56690          | 0                 | 0                 | -152.18259                          | 0.93084                              | 0.85252                              | -15.95954                     | -15.95954                 | 80.95          | 99.05          | 38.26          | 1.53008                 | 0.13415                 |
| $-H_2C-NH-C_2H_5$            | C <sub>u</sub> | -0.56690          | -0.92918          | 0                 | 0                 | -153.11177                          | 0.91771                              | 0.83360                              | -16.32183                     | -16.13097                 | 78.89          | 101.11         | 36.99          | 1.55650                 | 0.16057                 |
| $-H_2C-NH-C_2H_5$            | N              | -0.56690          | -0.56690          | 0                 | 0                 | -152.18259                          | 0.93084                              | 0.85252                              | -15.95954                     | -15.95954                 | 80.95          | 99.05          | 38.26          | 1.53008                 | 0.13415                 |
| $C-H (CH_3)$                 | C              | -0.92918          | 0                 | 0                 | 0                 | -152.44487                          | 0.91771                              | 0.86359                              | -15.75493                     | -15.56407                 | 77.49          | 102.51         | 41.48          | 1.23564                 | 0.18708                 |
| $C-H (CH_2)$                 | C              | -0.92918          | -0.92918          | 0                 | 0                 | -153.47406                          | 0.91771                              | 0.81549                              | -16.68412                     | -16.49325                 | 68.47          | 111.53         | 35.84          | 1.35466                 | 0.29933                 |
| $C-H (CH)$                   | C              | -0.92918          | -0.92918          | -0.92918          | 0                 | -154.40324                          | 0.91771                              | 0.77247                              | -17.61330                     | -17.42244                 | 61.10          | 118.90         | 31.37          | 1.42988                 | 0.37326                 |
| $H_2C-C_2H_5CH_2-$           | C <sub>u</sub> | -0.92918          | 0                 | 0                 | 0                 | -152.44487                          | 0.91771                              | 0.86359                              | -15.75493                     | -15.56407                 | 63.82          | 116.18         | 30.08          | 1.83879                 | 0.38106                 |
| $H_2C-C_2H_5CH_2-$           | C <sub>u</sub> | -0.92918          | -0.92918          | 0                 | 0                 | -153.47406                          | 0.91771                              | 0.81549                              | -16.68412                     | -16.49325                 | 56.41          | 123.59         | 26.06          | 1.90890                 | 0.45117                 |
| $(C-C (a))$                  | C <sub>u</sub> | -0.92918          | -0.92918          | -0.92918          | 0                 | -154.40324                          | 0.91771                              | 0.77247                              | -17.61330                     | -17.42244                 | 48.30          | 131.70         | 21.90          | 1.97162                 | 0.51388                 |
| $R-H_2C-C_2H_5CH_2-$         | C <sub>u</sub> | -0.92918          | -0.92918          | -0.92918          | 0                 | -154.40324                          | 0.91771                              | 0.77247                              | -17.61330                     | -17.42244                 | 48.30          | 131.70         | 21.90          | 1.97162                 | 0.51388                 |
| $(C-C (b))$                  | C <sub>u</sub> | -0.92918          | -0.92918          | -0.92918          | 0                 | -154.40324                          | 0.91771                              | 0.77247                              | -17.61330                     | -17.42244                 | 48.30          | 131.70         | 21.90          | 1.97162                 | 0.51388                 |
| $R-H_2C-C_2H_5CH_2-$         | C <sub>u</sub> | -0.92918          | -0.92918          | -0.92918          | 0                 | -154.40324                          | 0.91771                              | 0.77247                              | -17.61330                     | -17.42244                 | 48.30          | 131.70         | 21.90          | 1.97162                 | 0.51388                 |
| $(C-C (c))$                  | C <sub>u</sub> | -0.92918          | -0.92918          | -0.92918          | -0.72457          | -154.71860                          | 0.91771                              | 0.75889                              | -17.93866                     | -17.73779                 | 48.21          | 131.79         | 21.74          | 1.95734                 | 0.50570                 |
| $h_2C-C_2H_5CH_2-$           | C <sub>u</sub> | -0.92918          | -0.92918          | -0.92918          | 0                 | -154.40324                          | 0.91771                              | 0.77247                              | -17.61330                     | -17.42244                 | 48.30          | 131.70         | 21.90          | 1.97162                 | 0.51388                 |
| $(C-C (d))$                  | C <sub>u</sub> | -0.92918          | -0.92918          | -0.92918          | 0                 | -154.40324                          | 0.91771                              | 0.77247                              | -17.61330                     | -17.42244                 | 48.30          | 131.70         | 21.90          | 1.97162                 | 0.51388                 |
| $h_2C-C_2H_5CH_2-$           | C <sub>u</sub> | -0.92918          | -0.92918          | -0.92918          | -0.72457          | -154.51399                          | 0.91771                              | 0.76765                              | -17.92866                     | -17.73779                 | 50.04          | 129.96         | 22.66          | 1.94462                 | 0.49298                 |
| $(C-C (e))$                  | C <sub>u</sub> | -0.92918          | -0.92918          | -0.92918          | -0.72457          | -154.51399                          | 0.91771                              | 0.76765                              | -17.92866                     | -17.73779                 | 50.04          | 129.96         | 22.66          | 1.94462                 | 0.49298                 |
| $h_2C-C_2H_5CH_2-$           | C <sub>u</sub> | -0.92918          | -0.92918          | -0.92918          | 0                 | -154.40324                          | 0.91771                              | 0.77247                              | -17.61330                     | -17.42244                 | 48.30          | 131.70         | 21.90          | 1.97162                 | 0.51388                 |
| $(C-C (f))$                  | C <sub>u</sub> | -0.92918          | -0.92918          | -0.92918          | -0.72457          | -154.51399                          | 0.91771                              | 0.76765                              | -17.92866                     | -17.73779                 | 50.04          | 129.96         | 22.66          | 1.94462                 | 0.49298                 |
| $h_2C-C_2H_5CH_2-$           | C <sub>u</sub> | -0.92918          | -0.92918          | -0.92918          | -0.72457          | -154.51399                          | 0.91771                              | 0.76765                              | -17.92866                     | -17.73779                 | 50.04          | 129.96         | 22.66          | 1.94462                 | 0.49298                 |
| $(C-C (g))$                  | C <sub>u</sub> | -0.92918          | -0.92918          | -0.92918          | -0.72457          | -154.51399                          | 0.91771                              | 0.76765                              | -17.92866                     | -17.73779                 | 50.04          | 129.96         | 22.66          | 1.94462                 | 0.49298                 |

Table 15.78. The energy parameters (eV) of functional groups of secondary amines.

| Parameters                       | NH<br>Group | C-N (i)<br>Group | C-N (ii)<br>Group | CH <sub>3</sub><br>Group | CH <sub>2</sub><br>Group | C-H<br>Group | C-C (a)<br>Group | C-C (b)<br>Group | C-C (c)<br>Group | C-C (d)<br>Group | C-C (e)<br>Group | C-C (f)<br>Group |
|----------------------------------|-------------|------------------|-------------------|--------------------------|--------------------------|--------------|------------------|------------------|------------------|------------------|------------------|------------------|
| $\eta_1$                         | 1           | 1                | 1                 | 3                        | 2                        | 1            | 1                | 1                | 1                | 1                | 1                | 1                |
| $\eta_2$                         | 0           | 0                | 0                 | 2                        | 1                        | 0            | 0                | 0                | 0                | 0                | 0                | 0                |
| $\eta_3$                         | 0           | 0                | 0                 | 0                        | 0                        | 0            | 0                | 0                | 0                | 0                | 0                | 0                |
| $C_1$                            | 0.75        | 0.5              | 0.5               | 0.75                     | 0.75                     | 0.75         | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              |
| $C_2$                            | 0.93613     | 1                | 1                 | 1                        | 1                        | 1            | 1                | 1                | 1                | 1                | 1                | 1                |
| $C_3$                            | 0.75        | 1                | 1                 | 1                        | 1                        | 1            | 1                | 1                | 1                | 1                | 1                | 1                |
| $C_4$                            | 0.93383     | 0.91140          | 0.91140           | 0.91771                  | 0.91771                  | 0.91771      | 0.91771          | 0.91771          | 0.91771          | 0.91771          | 0.91771          | 0.91771          |
| $C_5$                            | 1           | 0                | 0                 | 0                        | 1                        | 1            | 0                | 0                | 0                | 1                | 1                | 0                |
| $C_6$                            | 1           | 2                | 2                 | 1                        | 1                        | 1            | 2                | 2                | 2                | 2                | 2                | 2                |
| $C_7$                            | 1           | 0                | 0                 | 3                        | 2                        | 1            | 0                | 0                | 0                | 0                | 0                | 0                |
| $C_8$                            | 0.75        | 1                | 1                 | 0.75                     | 0.75                     | 0.75         | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              |
| $C_{9a}$                         | 1           | 1                | 1                 | 1                        | 1                        | 1            | 1                | 1                | 1                | 1                | 1                | 1                |
| $C_{9b}$                         | 1           | 1                | 1                 | 1                        | 1                        | 1            | 1                | 1                | 1                | 1                | 1                | 1                |
| $V_1$ (eV)                       | -39.21967   | -31.98456        | -31.98456         | -107.32728               | -70.41425                | -35.12015    | -28.79214        | -28.79214        | -29.10112        | -28.79214        | -29.10112        | -29.10112        |
| $V_2$ (eV)                       | 14.30350    | 9.74677          | 9.74677           | 38.92728                 | 25.78002                 | 12.87680     | 9.33352          | 9.33352          | 9.37273          | 9.33352          | 9.37273          | 9.37273          |
| $V_3$ (eV)                       | 15.53581    | 8.20698          | 8.20698           | 32.53914                 | 21.06675                 | 10.48582     | 6.77464          | 6.77464          | 6.90500          | 6.77464          | 6.90500          | 6.90500          |
| $V_4$ (eV)                       | -7.76790    | -4.10349         | -4.10349          | -16.26957                | -10.53337                | -5.24291     | -3.38732         | -3.38732         | -3.45250         | -3.38732         | -3.45250         | -3.45250         |
| $V_5$ (eV)                       | -14.53414   | -14.63489        | -14.63489         | -15.56407                | -15.56407                | -14.63489    | -15.56407        | -15.56407        | -15.35946        | -15.56407        | -15.35946        | -15.35946        |
| $\Delta E_{H_{2s}, H_{2p}}$ (eV) | 0           | -1.13379         | -1.13379          | 0                        | 0                        | 0            | 0                | 0                | 0                | 0                | 0                | 0                |
| $E_{1s}^H$ (eV)                  | -14.53414   | -13.50110        | -13.50110         | -15.56407                | -15.56407                | -14.63489    | -15.56407        | -15.56407        | -15.35946        | -15.56407        | -15.35946        | -15.35946        |
| $E_{1s}^N$ (eV)                  | -31.63541   | -31.63540        | -31.63540         | -67.69451                | -49.66493                | -31.63533    | -31.63537        | -31.63537        | -31.63535        | -31.63537        | -31.63535        | -31.63535        |
| $E_{1s}^C$ (eV)                  | 0           | -1.13379         | -1.13379          | 0                        | 0                        | 0            | -1.85836         | -1.85836         | -1.44915         | -1.85836         | -1.44915         | -1.44915         |
| $E_{1s}^O$ (eV)                  | -31.63537   | -32.76916        | -32.76916         | -67.69450                | -49.66493                | -31.63537    | -33.49373        | -33.49373        | -33.08452        | -33.49373        | -33.08452        | -33.08452        |
| $\omega$ ( $10^6$ rad/s)         | 47.0696     | 15.1983          | 26.0778           | 24.9286                  | 24.2751                  | 24.1759      | 9.43699          | 9.43699          | 15.4846          | 9.43699          | 9.55643          | 9.55643          |
| $E_{1s}^N$ (eV)                  | 30.98202    | 10.00377         | 17.16484          | 16.40846                 | 15.97831                 | 15.91299     | 6.21159          | 6.21159          | 10.19220         | 6.21159          | 6.29021          | 6.29021          |
| $E_{1s}^O$ (eV)                  | -0.34836    | -0.20505         | -0.26859          | -0.25352                 | -0.25017                 | -0.24966     | -0.16515         | -0.16515         | -0.20896         | -0.16515         | -0.16416         | -0.16416         |
| $E_{1s}^C$ (eV)                  | 0.40696     | 0.12944          | 0.11159           | 0.35532                  | 0.35532                  | 0.35532      | 0.12312          | 0.12312          | 0.09944          | 0.12312          | 0.12312          | 0.12312          |
| $E_{1s}^N$ (eV)                  | -0.14488    | -0.14033         | -0.21280          | -0.22757                 | -0.14502                 | -0.07200     | -0.10359         | -0.07526         | -0.15924         | -0.10359         | -0.10260         | -0.10260         |
| $E_{1s}^O$ (eV)                  | 0.14803     | 0.14803          | 0.14803           | 0.14803                  | 0.14803                  | 0.14803      | 0.14803          | 0.14803          | 0.14803          | 0.14803          | 0.14803          | 0.14803          |
| $E_{1s}^C$ (eV)                  | -31.78025   | -32.90949        | -32.98196         | -67.92207                | -49.80996                | -31.70737    | -33.59732        | -33.49373        | -33.24376        | -33.59732        | -33.18712        | -33.18712        |
| $E_{1s}^N$ (eV)                  | -14.53414   | -14.63489        | -14.63489         | -14.63489                | -14.63489                | -14.63489    | -14.63489        | -14.63489        | -14.63489        | -14.63489        | -14.63489        | -14.63489        |
| $E_{1s}^O$ (eV)                  | -13.59844   | 0                | 0                 | -13.59844                | -13.59844                | -13.59844    | 0                | 0                | 0                | 0                | 0                | 0                |
| $E_{1s}^C$ (eV)                  | 3.50582     | 3.63971          | 3.71218           | 12.49186                 | 7.83016                  | 3.32601      | 4.32754          | 4.29921          | 3.97598          | 4.17951          | 3.62128          | 3.91734          |

Table 15.79. The total bond energies of secondary amines calculated using the functional group composition and the energies of Table 15.78 compared to the experimental values [3].

| Formula                          | Name             | NH<br>Group | C-N (i)<br>Group | C-N (ii)<br>Group | CH <sub>3</sub><br>Group | CH <sub>2</sub><br>Group | C-H<br>Group | C-C (a)<br>Group | C-C (b)<br>Group | C-C (c)<br>Group | C-C (d)<br>Group | C-C (e)<br>Group | C-C (f)<br>Group | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|----------------------------------|------------------|-------------|------------------|-------------------|--------------------------|--------------------------|--------------|------------------|------------------|------------------|------------------|------------------|------------------|-----------------------------------------|-------------------------------------------|----------------|
| CH <sub>3</sub> N                | Dimethylamine    | 1           | 2                | 0                 | 2                        | 0                        | 0            | 0                | 0                | 0                | 0                | 0                | 0                | 35.76855                                | 35.765                                    | -0.00012       |
| C <sub>2</sub> H <sub>5</sub> N  | Diethylamine     | 1           | 0                | 2                 | 2                        | 2                        | 0            | 0                | 0                | 0                | 0                | 0                | 0                | 60.22910                                | 60.211                                    | -0.00030       |
| C <sub>3</sub> H <sub>7</sub> N  | Dipropylamine    | 1           | 0                | 2                 | 2                        | 4                        | 0            | 0                | 0                | 0                | 0                | 0                | 0                | 84.54770                                | 84.558                                    | 0.00016        |
| C <sub>4</sub> H <sub>9</sub> N  | Diisopropylamine | 1           | 0                | 2                 | 4                        | 0                        | 4            | 0                | 0                | 0                | 0                | 0                | 0                | 84.74648                                | 84.846                                    | 0.00117        |
| C <sub>5</sub> H <sub>11</sub> N | Dibutylamine     | 1           | 0                | 2                 | 2                        | 6                        | 0            | 0                | 0                | 0                | 0                | 0                | 0                | 108.86010                               | 108.872                                   | 0.00011        |
| C <sub>6</sub> H <sub>13</sub> N | Diisobutylamine  | 1           | 0                | 2                 | 4                        | 2                        | 2            | 6                | 0                | 0                | 0                | 0                | 0                | 109.00322                               | 109.106                                   | 0.00092        |



TERTIARY AMINES ( $C_nH_{2n+3}N$ ,  $n = 3, 4, 5 \dots \infty$ )

The tertiary amines,  $C_nH_{2n+3}N$ , have three  $C-N$  bonds to methyl or alkyl groups wherein  $C-N$  comprises a functional group. The alkyl portion of the tertiary amine may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise  
 5 methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl,  
 10 and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in tertiary amines are equivalent to those in branched-chain alkanes.

The  $C-N$  group is solved by hybridizing the  $2s$  and  $2p$  AOs of the  $C$  atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the  $N$  AO to form a MO permits each participating orbital to decrease in radius and energy.  
 15 In tertiary amines, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)), and the  $N$  AO has an energy of  $E(N) = -14.53414 \text{ eV}$ . To meet the equipotential condition of the union of the  $C-N$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the  $C-N$ -bond MO given by Eq. (15.116) is  $c_2(C2sp^3 \text{ HO to N}) = 0.91140$ .

20 As given in the Continuous-Chain Alkanes ( $C_nH_{2n+2}$ ,  $n = 3, 4, 5 \dots \infty$ ) section, the energy of each  $C2sp^3$  HO must be a linear combination of that of the  $CH_3$  and  $CH_2$  groups that serve as basis elements. Each  $CH_3$  forms one  $C-C$  bond, and each  $CH_2$  group forms two. Thus, the energy of each  $C2sp^3$  HO of each  $CH_3$  and  $CH_2$  group alone is given by that in ethane,  $-0.72457 \text{ eV}$  (Eq. (14.151)), and ethylene,  $-1.13379 \text{ eV}$  (Eq. (14.511)), respectively. In order  
 25 to match the energy of the component HOs and MOs for the entire molecule, the energy  $E_{T_{alkane}}(C-C, 2sp^3)$  given as a linear combination of these basis elements is  $-0.92918 \text{ eV}$  (Eq. (14.513)). In tertiary amines, the  $N$  binds to three  $C2sp^3$  HOs and the corresponding  $E_T(atom - atom, msp^3 \cdot AO)$  of each  $C-N$ -bond MO in Eq. (15.52) due to the charge donation

from the *C* and *N* atoms to the MO is  $-0.92918\text{ eV}$ . It comprises a linear combination of the energy for a primary amine,  $-0.72457\text{ eV}$  and a secondary amine,  $-1.13379\text{ eV}$ .

The symbols of the functional groups of branched-chain tertiary amines are given in Table 15.81. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and  
5 energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of tertiary amines are given in Tables 15.82, 15.83, and 15.84, respectively. The total energy of each tertiary amine given in Table 15.85 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.84 corresponding to functional-group composition of the molecule. The bond angle parameters of tertiary amines determined using Eqs. (15.79-15.108) are given in Table 15.86.

Table 15.81. The symbols of functional groups of tertiary amines.

| Functional Group      | Group Symbol           |
|-----------------------|------------------------|
| C-N                   | C-N                    |
| CH <sub>3</sub> group | C-H (CH <sub>3</sub> ) |
| CH <sub>2</sub> group | C-H (CH <sub>2</sub> ) |
| CH                    | C-H                    |
| CC bond (n-C)         | C'-C' (a)              |
| CC bond (iso-C)       | C'-C' (b)              |
| CC bond (tert-C)      | C'-C' (c)              |
| CC (iso to iso-C)     | C'-C' (d)              |
| CC (t to t-C)         | C'-C' (e)              |
| CC (t to iso-C)       | C'-C' (f)              |

Table 15.82. The geometrical bond parameters of tertiary amines and experimental values [1].

| Parameter            | C-N Group              | C-H (CH <sub>3</sub> ) Group              | C-H (CH <sub>2</sub> ) Group              | C-H Group         | C'-C' (a) Group                   | C'-C' (b) Group                   | C'-C' (c) Group                   | C'-C' (d) Group                   | C'-C' (e) Group                   | C'-C' (f) Group                   |
|----------------------|------------------------|-------------------------------------------|-------------------------------------------|-------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| $\alpha$ (°)         | 1.96313                | 1.64920                                   | 1.67122                                   | 1.67465           | 2.12499                           | 2.12499                           | 2.10725                           | 2.12499                           | 2.10725                           | 2.10725                           |
| $\alpha'$ (°)        | 1.40112                | 1.04856                                   | 1.05553                                   | 1.05661           | 1.45744                           | 1.45744                           | 1.45164                           | 1.45744                           | 1.45164                           | 1.45164                           |
| Bond Length, 2c' (Å) | 1.48288                | 1.10974                                   | 1.11713                                   | 1.11827           | 1.54280                           | 1.54280                           | 1.53635                           | 1.54280                           | 1.53635                           | 1.53635                           |
| Exp. Bond Length (Å) | 1.458 (trimethylamine) | 1.107 (C-H propane)<br>1.117 (C-H butane) | 1.107 (C-H propane)<br>1.117 (C-H butane) | 1.122 (isobutane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) |
| $h, c$ (°)           | 1.37505                | 1.27295                                   | 1.29569                                   | 1.29924           | 1.54616                           | 1.54616                           | 1.52750                           | 1.54616                           | 1.52750                           | 1.52750                           |
| $e$                  | 0.71372                | 0.63580                                   | 0.63159                                   | 0.62095           | 0.68600                           | 0.68600                           | 0.68888                           | 0.68600                           | 0.68888                           | 0.68888                           |

Table 15.83. The MO to HO intercept geometrical bond parameters of tertiary amines.  $R, R', R''$  are H or alkyl groups.  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{msp}^3, \text{AO})$ .

| Bond                               | Atom           | $E_r$<br>(eV)<br>Bond 1 | $E_r$<br>(eV)<br>Bond 2 | $E_r$<br>(eV)<br>Bond 3 | $E_r$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>C2sp <sup>3</sup><br>(eV) | $r_{\text{final}}$<br>(a <sub>0</sub> ) | $E_{\text{orbital}}$<br>(eV)<br>Final | $E(\text{C2sp}^3)$<br>(eV)<br>Final | $\theta^*$<br>(°) | $\theta_1$<br>(°) | $\theta_2$<br>(°) | $d_1$<br>(a <sub>0</sub> ) | $d_2$<br>(a <sub>0</sub> ) |
|------------------------------------|----------------|-------------------------|-------------------------|-------------------------|-------------------------|----------------------------------------------------|-----------------------------------------|---------------------------------------|-------------------------------------|-------------------|-------------------|-------------------|----------------------------|----------------------------|
| $N-(C_2H_5)_3$                     | C <sub>2</sub> | -0.46459                |                         | 0                       | 0                       | -152.08028                                         | 0.91771                                 | -15.28034                             | -15.09948                           | 83.37             | 96.63             | 40.00             | 1.50383                    | 0.10271                    |
| $N-(C_2H_5)_3$                     | N              | -0.46459                | -0.46459                | -0.46459                | 0                       | -152.08028                                         | 0.93084                                 | -16.21953                             | -16.02866                           | 78.02             | 101.98            | 36.64             | 1.57525                    | 0.17413                    |
| $N-(C_2H_5)_3$                     | C <sub>2</sub> | -0.46459                | -0.92918                | 0                       | 0                       | -153.09946                                         | 0.91771                                 | -16.21953                             | -16.02866                           | 78.02             | 101.98            | 36.64             | 1.57525                    | 0.17413                    |
| $N-(C_2H_5)_3$                     | N              | -0.46459                | -0.46459                | -0.46459                | 0                       | -152.08028                                         | 0.93084                                 | -16.21953                             | -16.02866                           | 78.02             | 101.98            | 36.64             | 1.57525                    | 0.17413                    |
| $C-H (CH_3)$                       | C              | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                         | 0.91771                                 | -15.75493                             | -15.56407                           | 77.49             | 102.51            | 41.48             | 1.25564                    | 0.18708                    |
| $C-H (CH_3)$                       | C              | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                         | 0.91771                                 | -16.68412                             | -16.49325                           | 68.47             | 111.53            | 35.84             | 1.35486                    | 0.29933                    |
| $C-H (CH)$                         | C              | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                         | 0.91771                                 | -17.61330                             | -17.42244                           | 61.10             | 118.90            | 31.37             | 1.42988                    | 0.37226                    |
| $H_2C_2C_2H_2CH_2-$<br>(C-C (a))   | C <sub>2</sub> | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                         | 0.91771                                 | -15.75493                             | -15.56407                           | 63.82             | 116.18            | 30.08             | 1.83879                    | 0.38106                    |
| $H_2C_2C_2H_2CH_2-$<br>(C-C (a))   | C <sub>2</sub> | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                         | 0.91771                                 | -16.68412                             | -16.49325                           | 56.41             | 123.59            | 26.06             | 1.90890                    | 0.45117                    |
| $R-H_2C_2C_2H_2CH_2-$<br>(C-C (b)) | C <sub>2</sub> | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                         | 0.91771                                 | -17.61330                             | -17.42244                           | 48.30             | 131.70            | 21.90             | 1.97162                    | 0.51388                    |
| $R-H_2C_2C_2H_2CH_2-$<br>(C-C (b)) | C <sub>2</sub> | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -154.71860                                         | 0.91771                                 | -17.92866                             | -17.73779                           | 48.21             | 131.79            | 21.74             | 1.95734                    | 0.50270                    |
| $isoC_2C_2H_2CH_2-$<br>(C-C (d))   | C <sub>2</sub> | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                         | 0.91771                                 | -17.61330                             | -17.42244                           | 48.30             | 131.70            | 21.90             | 1.97162                    | 0.51388                    |
| $isoC_2C_2H_2CH_2-$<br>(C-C (e))   | C <sub>2</sub> | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.51399                                         | 0.91771                                 | -17.92866                             | -17.73779                           | 50.04             | 129.96            | 22.66             | 1.94462                    | 0.49298                    |
| $isoC_2C_2H_2CH_2-$<br>(C-C (f))   | C <sub>2</sub> | -0.72457                | -0.92918                | -0.92918                | 0                       | -154.19863                                         | 0.91771                                 | -17.40869                             | -17.21783                           | 52.78             | 127.22            | 24.04             | 1.92443                    | 0.47279                    |
| $isoC_2C_2H_2CH_2-$<br>(C-C (f))   | C <sub>2</sub> | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.51399                                         | 0.91771                                 | -17.92866                             | -17.73779                           | 50.04             | 129.96            | 22.66             | 1.94462                    | 0.49298                    |

Table 15.84. The energy parameters (eV) of functional groups of tertiary amines.

| Parameters                       | C-N<br>Group | (H <sub>3</sub> )<br>Group | CH <sub>2</sub><br>Group | C-H<br>Group   | C-C (a)<br>Group | C-C (b)<br>Group | C-C (c)<br>Group | C-C (d)<br>Group | C-C (e)<br>Group | C-C (f)<br>Group |
|----------------------------------|--------------|----------------------------|--------------------------|----------------|------------------|------------------|------------------|------------------|------------------|------------------|
| $\eta_1$                         | 1            | 3                          | 2                        | 1              | 1                | 1                | 1                | 1                | 1                | 1                |
| $\eta_2$                         | 0            | 2                          | 1                        | 0              | 0                | 0                | 0                | 0                | 0                | 0                |
| $\eta_3$                         | 0            | 0                          | 0                        | 0              | 0                | 0                | 0                | 0                | 0                | 0                |
| $C_1$                            | 0.5          | 0.75                       | 0.75                     | 0.75           | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              |
| $C_2$                            | 1            | 1                          | 1                        | 1              | 1                | 1                | 1                | 1                | 1                | 1                |
| $C_3$                            | 1            | 1                          | 1                        | 1              | 1                | 1                | 1                | 1                | 1                | 1                |
| $C_4$                            | 0.91140      | 0.91771                    | 0.91771                  | 0.91771        | 0.91771          | 0.91771          | 0.91771          | 0.91771          | 0.91771          | 0.91771          |
| $C_5$                            | 0            | 0                          | 1                        | 1              | 0                | 0                | 0                | 1                | 1                | 0                |
| $C_6$                            | 2            | 1                          | 1                        | 1              | 2                | 2                | 2                | 2                | 2                | 2                |
| $C_7$                            | 0            | 3                          | 2                        | 1              | 0                | 0                | 0                | 0                | 0                | 0                |
| $C_{10}$                         | 0.5          | 0.75                       | 0.75                     | 0.75           | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              |
| $C_{11}$                         | 1            | 1                          | 1                        | 1              | 1                | 1                | 1                | 1                | 1                | 1                |
| $V_e$ (eV)                       | -31.67393    | -107.32728                 | -70.41425                | -35.12015      | -28.79214        | -28.79214        | -28.79214        | -28.79214        | -28.79214        | -28.79214        |
| $V_p$ (eV)                       | 9.71067      | 38.92728                   | 25.78002                 | 12.87680       | 9.33352          | 9.33352          | 9.33352          | 9.33352          | 9.33352          | 9.33352          |
| $T$ (eV)                         | 8.06719      | 32.53914                   | 21.06675                 | 10.48582       | 6.77464          | 6.77464          | 6.77464          | 6.77464          | 6.77464          | 6.77464          |
| $V_u$ (eV)                       | -4.03359     | -16.26957                  | -10.53337                | -5.24291       | -3.38732         | -3.38732         | -3.38732         | -3.38732         | -3.38732         | -3.38732         |
| $E_{12,12}$ (eV)                 | -14.63489    | -15.56407                  | -15.56407                | -14.63489      | -15.56407        | -15.56407        | -15.56407        | -15.56407        | -15.56407        | -15.56407        |
| $\Delta E_{12,12}$ (eV)          | 0            | 0                          | 0                        | 0              | 0                | 0                | 0                | 0                | 0                | 0                |
| $E_{12,12}$ (eV)                 | -13.70571    | -15.56407                  | -15.56407                | -14.63489      | -15.56407        | -15.56407        | -15.56407        | -15.56407        | -15.56407        | -15.56407        |
| $E_{12,12}$ (eV)                 | -31.63537    | -67.69451                  | -49.66493                | -31.63533      | -31.63537        | -31.63537        | -31.63537        | -31.63537        | -31.63537        | -31.63537        |
| $E_{12,12}$ (eV)                 | -0.92918     | 0                          | 0                        | 0              | -1.85836         | -1.85836         | -1.85836         | -1.85836         | -1.85836         | -1.85836         |
| $E_{12,12}$ (eV)                 | -32.56455    | -67.69450                  | -49.66493                | -31.63537      | -33.49373        | -33.49373        | -33.49373        | -33.49373        | -33.49373        | -33.49373        |
| $\omega$ (10 <sup>8</sup> rad/s) | 18.1298      | 24.9286                    | 24.2751                  | 24.1759        | 9.43699          | 9.43699          | 9.43699          | 9.43699          | 9.43699          | 9.43699          |
| $E_{12}$ (eV)                    | 11.93333     | 16.40846                   | 15.97831                 | 15.91299       | 6.21159          | 6.21159          | 6.21159          | 6.21159          | 6.21159          | 6.21159          |
| $E_{12}$ (eV)                    | -0.22255     | -0.25352                   | -0.25017                 | -0.24966       | -0.16515         | -0.16515         | -0.16515         | -0.16515         | -0.16515         | -0.16515         |
| $E_{12}$ (eV)                    | 0.12944      | 0.35532                    | 0.35532                  | 0.35532        | 0.12312          | 0.12312          | 0.12312          | 0.12312          | 0.12312          | 0.12312          |
| $E_{12}$ (eV)                    | [23]         | (Eq. (13.458))             | (Eq. (13.458))           | (Eq. (13.458)) | [2]              | [4]              | [5]              | [2]              | [2]              | [2]              |
| $E_{12}$ (eV)                    | -0.15783     | -0.22757                   | -0.14502                 | -0.07200       | -0.10359         | -0.07526         | -0.15924         | -0.10359         | -0.10359         | -0.10359         |
| $E_{12}$ (eV)                    | 0.14803      | 0.14803                    | 0.14803                  | 0.14803        | 0.14803          | 0.14803          | 0.14803          | 0.14803          | 0.14803          | 0.14803          |
| $E_{12}$ (eV)                    | -32.72238    | -67.92207                  | -49.80996                | -31.70737      | -33.59732        | -33.59732        | -33.59732        | -33.59732        | -33.59732        | -33.59732        |
| $E_{12}$ (eV)                    | -14.63489    | -14.63489                  | -14.63489                | -14.63489      | -14.63489        | -14.63489        | -14.63489        | -14.63489        | -14.63489        | -14.63489        |
| $E_{12}$ (eV)                    | 0            | -13.59844                  | -13.59844                | -13.59844      | 0                | 0                | 0                | 0                | 0                | 0                |
| $E_{12}$ (eV)                    | 3.45260      | 12.49186                   | 7.83016                  | 3.32601        | 4.32754          | 4.29921          | 3.97398          | 4.17951          | 3.62128          | 3.91734          |

Table 15.85. The total bond energies of tertiary amines calculated using the functional group composition and the energies of Table 15.84 compared to the experimental values [3].

| Formula                          | Name           | C-N<br>Group | (H <sub>3</sub> )<br>Group | CH <sub>2</sub><br>Group | C-H<br>Group | C-C (a)<br>Group | C-C (b)<br>Group | C-C (c)<br>Group | C-C (d)<br>Group | C-C (e)<br>Group | C-C (f)<br>Group | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative<br>Error |
|----------------------------------|----------------|--------------|----------------------------|--------------------------|--------------|------------------|------------------|------------------|------------------|------------------|------------------|-----------------------------------------|-------------------------------------------|-------------------|
| C <sub>3</sub> H <sub>9</sub> N  | Trimethylamine | 3            | 3                          | 0                        | 0            | 0                | 0                | 0                | 0                | 0                | 0                | 47.83338                                | 47.761                                    | -0.00152          |
| C <sub>6</sub> H <sub>15</sub> N | Triethylamine  | 3            | 3                          | 3                        | 0            | 3                | 0                | 0                | 0                | 0                | 0                | 84.30648                                | 84.316                                    | 0.00012           |
| C <sub>9</sub> H <sub>21</sub> N | Tripropylamine | 3            | 3                          | 6                        | 0            | 6                | 0                | 0                | 0                | 0                | 0                | 120.77958                               | 120.864                                   | 0.00070           |



Table 15.86. The bond angle parameters of tertiary amines and experimental values [1]. In the calculation of  $\theta_i$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{mp}, \text{AO})$ .

| Atoms at Angle                                                                    | $2c'$<br>Bond 1 ( $a_0$ ) | $2c'$<br>Bond 2 ( $a_0$ ) | $2c'$<br>Terminal Atoms<br>( $a_0$ ) | $E_{\text{calculation}}$<br>or<br>$E$<br>Atom 1 | Atom 1<br>Hybridization<br>Designation<br>(Table 15.3.A) | $E_{\text{calculation}}$<br>Atom 2 | Atom 2<br>Hybridization<br>Designation<br>(Table 15.3.A) | $c_2$<br>Atom 1 | $c_2$<br>Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c'_2$  | $E_T$<br>(eV) | $\theta_i$<br>( $^\circ$ ) | $\theta_j$<br>( $^\circ$ ) | Cal. $\theta$<br>( $^\circ$ ) | Exp. $\theta$<br>( $^\circ$ ) |
|-----------------------------------------------------------------------------------|---------------------------|---------------------------|--------------------------------------|-------------------------------------------------|----------------------------------------------------------|------------------------------------|----------------------------------------------------------|-----------------|-----------------|-------|-------|-------|---------|---------------|----------------------------|----------------------------|-------------------------------|-------------------------------|
| $\angle \text{NC}$                                                                | 2.80224                   | 2.80224                   | 4.6043                               | -17.14871                                       | I                                                        | -17.14871                          | 6                                                        | 0.79340         | 0.79340         | I     | I     | I     | 0.79340 | -1.85836      |                            |                            | 110.48                        | 110.9<br>(trimethylamine)     |
| Methylene<br>$\angle \text{HC}_\alpha \text{H}$                                   | 2.11106                   | 2.11106                   | 3.4252                               | -15.75493                                       | 7                                                        | H                                  | H                                                        | 0.86359         | I               | I     | I     | 0.75  | 1.15796 | 0             |                            |                            | 103.44                        | 107<br>(dimethylamine)        |
| $\angle \text{C}_\alpha \text{C}_\beta \text{C}_\gamma$                           |                           |                           |                                      |                                                 |                                                          |                                    |                                                          |                 |                 |       |       |       |         |               |                            |                            |                               | 112<br>(propane)              |
| $\angle \text{C}_\alpha \text{C}_\beta \text{H}$                                  |                           |                           |                                      |                                                 |                                                          |                                    |                                                          |                 |                 |       |       |       |         |               | 69.51                      |                            | 110.49                        | 113.8<br>(butane)             |
| Methyl<br>$\angle \text{HC}_\alpha \text{H}$                                      | 2.09711                   | 2.09711                   | 3.4252                               | -15.75493                                       | 7                                                        | H                                  | H                                                        | 0.86359         | I               | I     | I     | 0.75  | 1.15796 | 0             |                            |                            | 110.49                        | 110.8<br>(isobutane)          |
| $\angle \text{C}_\alpha \text{C}_\beta \text{C}_\gamma$                           |                           |                           |                                      |                                                 |                                                          |                                    |                                                          |                 |                 |       |       |       |         |               | 69.51                      |                            |                               | 111.0<br>(butane)             |
| $\angle \text{C}_\alpha \text{C}_\beta \text{H}$                                  |                           |                           |                                      |                                                 |                                                          |                                    |                                                          |                 |                 |       |       |       |         |               |                            |                            |                               | 111.4<br>(isobutane)          |
| $\angle \text{C}_\alpha \text{C}_\beta \text{C}_\gamma$<br>iso $\text{C}_\alpha$  | 2.91547                   | 2.91547                   | 4.7958                               | -16.68412                                       | 25                                                       | $\text{C}_\gamma$                  | 25                                                       | 0.81549         | 0.81549         | I     | I     | I     | 0.81549 | -1.85836      |                            |                            | 110.67                        | 110.8<br>(isobutane)          |
| $\angle \text{C}_\alpha \text{C}_\beta \text{H}$<br>iso $\text{C}_\alpha$         | 2.91547                   | 2.11323                   | 4.1633                               | -15.55033                                       | 5                                                        | $\text{C}_\alpha$                  | 1                                                        | 0.87495         | 0.91771         | 0.75  | I     | 0.75  | 1.04887 | 0             |                            |                            | 110.76                        |                               |
| $\angle \text{C}_\alpha \text{C}_\beta \text{H}$<br>iso $\text{C}_\alpha$         | 2.91547                   | 2.09711                   | 4.1633                               | -15.55033                                       | 5                                                        | $\text{C}_\alpha$                  | 1                                                        | 0.87495         | 0.91771         | 0.75  | I     | 0.75  | 1.04887 | 0             |                            |                            | 111.27                        | 111.4<br>(isobutane)          |
| $\angle \text{C}_\alpha \text{C}_\beta \text{C}_\gamma$<br>test $\text{C}_\alpha$ | 2.90327                   | 2.90327                   | 4.7958                               | -15.55033                                       | 5                                                        | $\text{C}_\alpha$                  | 1                                                        | 0.87495         | 0.91771         | 0.75  | I     | 0.75  | 1.04887 | -1.85836      |                            |                            | 111.27                        | 111.4<br>(isobutane)          |
| $\angle \text{C}_\alpha \text{C}_\beta \text{C}_\gamma$                           |                           |                           |                                      |                                                 |                                                          |                                    |                                                          |                 |                 |       |       |       |         |               | 72.50                      |                            | 107.50                        |                               |

ALDEHYDES ( $C_nH_{2n}O$ ,  $n = 1, 2, 3, 4, 5 \dots \infty$ )

The alkyl aldehydes,  $C_nH_{2n}O$ , each have a  $HC=O$  moiety that comprises a  $C=O$  functional group and a  $CH$  functional group. The single bond of carbon to the carbonyl carbon atom,  $C-C(O)H$ , is a functional group. In addition to the  $C=O$  functional group, 5 formaldehyde comprises a  $CH_2$  functional group. The alkyl portion of the alkyl aldehyde may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond 10 is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in aldehydes are equivalent to those in branched-chain alkanes.

The  $CH$  functional group was solved in the Hydrogen Carbide ( $CH$ ) section except that 15  $E_{mag}$  is not subtracted since unpaired electrons are not created with fragmentation of the  $CH$  functional group of aldehydes. The  $CH_2$  functional group of formaldehyde is solved in the Dihydrogen Carbide ( $CH_2$ ) section except that the energy of each  $C-H$  MO is matched to the initial energy of the  $C2sp^3$  HO (Eq. (15.25)). The  $C=O$  and  $C-C(O)H$  groups are solved by hybridizing the  $2s$  and  $2p$  AOs of each  $C$  atom to form a single  $2sp^3$  shell as an energy 20 minimum, and the sharing of electrons between the  $C2sp^3$  HO and the  $O$  AO or between two  $C2sp^3$  HOs, respectively, to form a MO permits each participating orbital to decrease in radius and energy. In alkyl aldehydes, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)) and the  $O$  AO has an energy of  $E(O) = -13.61806 \text{ eV}$ . To meet the equipotential condition of the union 25 of the  $C=O$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the  $C=O$ -bond MO given by Eq. (15.114) is  $c_2(C2sp^3HO \text{ to } O) = 0.85395$ . The unpaired electrons created by bond breakage of the double  $C=O$  bond requires that two times

the  $O2p$  AO magnetic energy  $E_{mag}$  (Eq. (15.60)) be subtracted from the total energy to give  $E_D(\text{Group})$  (eV) for  $C = O$ .

$E_T(\text{atom} - \text{atom}, msp^3.AO)$  of the  $C = O$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $O$  atoms to the MO is  $-2.69893$  eV which is an energy minimum for the double bond between the pair of  $C2sp^3$  HO electrons of the  $C$  atom and the pair of AO electrons of the  $O$  atom. It is given as a linear combination of the energy contributions corresponding to a double bond,  $-1.13379$  eV (Eq. (14.247)), and a triple bond,  $-1.56513$  eV (Eq. (14.342)). The triple bond contribution includes the  $C2sp^3$  HO electron of the  $C - H$  bond in addition to the pair involved directly in the double bond with  $O$ .

$E_T(\text{atom} - \text{atom}, msp^3.AO)$  of the  $C - C(O)H$  group is equivalent to that of an alkane,  $-1.85836$  eV, where both energy contributions are given by Eq. (14.513). It is based on the energy match between the  $C2sp^3$  HOs of the aldehyde. In order to match energy between the groups bonded to the  $C = O$ , electron-density is shared. Due to the interaction in the transition state between the groups based on the sharing,  $C_{1o} = 2C_1$  rather than  $C_{1o} = C_1$  in Eq. (15.52) for the  $C - C(O)H$  bond.

The symbols of the functional groups of alkyl aldehydes are given in Table 15.87. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl aldehydes are given in Tables 15.88, 15.89, and 15.90, respectively. The total energy of each alkyl aldehyde given in Table 15.91 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.90 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl aldehydes determined using Eqs. (15.79-15.108) are given in Table 15.92.

Table 15.87. The symbols of functional groups of alkyl aldehydes.

| Functional Group                     | Group Symbol        |
|--------------------------------------|---------------------|
| CH <sub>2</sub> (formaldehyde) group | $C - H (CH_2)$ (i)  |
| CH (aldehyde) group                  | $CH$ (i)            |
| C=O                                  | $C = O$ (i)         |
| C-C(O)H                              | $C - C(O)H$         |
| CH <sub>3</sub> group                | $C - H (CH_3)$      |
| CH <sub>2</sub> (alkyl) group        | $C - H (CH_2)$ (ii) |
| CH (alkyl)                           | $C - H$ (ii)        |
| CC bond (n-C)                        | $C - C$ (a)         |
| CC bond (iso-C)                      | $C - C$ (b)         |
| CC bond (tert-C)                     | $C - C$ (c)         |
| CC (iso to iso-C)                    | $C - C$ (d)         |
| CC (t to t-C)                        | $C - C$ (e)         |
| CC.(t to iso-C)                      | $C - C$ (f)         |

Table 15.88. The geometrical bond parameters of alkyl aldehydes and experimental values [1].

| Parameter            | $C-H$ (i)            | $C=O$ Group          | $C-C(O)H$ Group      | $C-H$ (CH <sub>2</sub> ) Group | $C-H$ (CH <sub>3</sub> ) Group | $C-H$ (CH <sub>2</sub> ) Group | $C-H$ (i)         | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|----------------------|----------------------|----------------------|----------------------|--------------------------------|--------------------------------|--------------------------------|-------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $a$ (Å)              | 1.64010              | 1.29907              | 2.04740              | 1.64920                        | 1.67122                        | 1.67465                        | 1.67465           | 2.12499         | 2.12499         | 2.10725         | 2.12499         | 2.10725         | 2.10725         |
| $c'$ (Å)             | 1.04566              | 1.13977              | 1.43087              | 1.04856                        | 1.05553                        | 1.05661                        | 1.05661           | 1.45744         | 1.45744         | 1.45164         | 1.45744         | 1.45164         | 1.45164         |
| Bond Length          | 1.10668              | 1.20628              | 1.51437              | 1.10974                        | 1.11713                        | 1.11827                        | 1.11827           | 1.54280         | 1.54280         | 1.53635         | 1.54280         | 1.53635         | 1.53635         |
| $2c'$ (Å)            | 1.116 (formaldehyde) | 1.208 (formaldehyde) | 1.515 (acetaldehyde) | 1.117 (C-H propane)            | 1.107 (C-H propane)            | 1.122 (isobutane)              | 1.122 (isobutane) | 1.532 (propane) | 1.532 (propane) | 1.532 (propane) | 1.532 (propane) | 1.532 (propane) | 1.532 (propane) |
| Exp. Bond Length (Å) | 1.116 (formaldehyde) | 1.210 (acetaldehyde) | 1.515 (acetaldehyde) | 1.117 (C-H propane)            | 1.107 (C-H propane)            | 1.122 (isobutane)              | 1.122 (isobutane) | 1.531 (butane)  | 1.531 (butane)  | 1.531 (butane)  | 1.531 (butane)  | 1.531 (butane)  | 1.531 (butane)  |
| $h_{c'}$ (Å)         | 1.26354              | 0.62331              | 1.46439              | 1.27295                        | 1.29569                        | 1.29924                        | 1.29924           | 1.54616         | 1.54616         | 1.52750         | 1.54616         | 1.52750         | 1.52750         |
| $e$                  | 0.63756              | 0.87737              | 0.69887              | 0.63580                        | 0.63159                        | 0.63095                        | 0.63095           | 0.68600         | 0.68600         | 0.68888         | 0.68600         | 0.68888         | 0.68888         |

Table 15.89. The MO to HO intercept geometrical bond parameters of alkyl aldehydes.  $R, R', R''$  are H or alkyl groups.  $E_T$  is  $E_T$  (atom-atom, nsp<sup>3</sup> AO).

| Bond                              | Atom | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Energy (eV) | $r_{final}$ (Å) | $r_{initial}$ (Å) | $E_{centr}$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ (Å) | $d_2$ (Å) |
|-----------------------------------|------|-------------------|-------------------|-------------------|-------------------|-------------------|-----------------|-------------------|------------------------|------------------------|---------------|----------------|----------------|-----------|-----------|
| $H-C(O)-H$ (CH <sub>2</sub> ) (i) | C'   | -1.34946          | 0                 | 0                 | 0                 | -152.96515        | 0.91771         | 0.84115           | -16.17521              | -15.98435              | 75.72         | 104.28         | 40.18          | 1.25314   | 0.20748   |
| $-C(H_2C_2O)-H$ (CH) (i)          | C'   | -1.34946          | -0.92918          | 0                 | 0                 | -153.89434        | 0.91771         | 0.79546           | -17.10440              | -16.91353              | 64.95         | 115.05         | 33.69          | 1.39345   | 0.33684   |
| $H_2C=O$                          | O    | -1.34946          | 0                 | 0                 | 0                 | 1.00000           | 0.84115         | 0.84115           | -16.17521              |                        | 137.27        | 42.73          | 66.31          | 0.52193   | 0.61784   |
| $-CH_2CH_2-C(H)(O)$               | C'   | -1.34946          | -0.92918          | 0                 | 0                 | -153.89434        | 0.91771         | 0.79546           | -17.10440              | -16.91353              | 137.27        | 42.73          | 66.31          | 0.52193   | 0.61784   |
| $H_2C_2-C(H)(O)$                  | C'   | -0.92918          | 0                 | 0                 | 0                 | -153.54487        | 0.91771         | 0.86359           | -15.75493              | -15.56407              | 72.27         | 107.73         | 34.17          | 1.69388   | 0.26301   |
| $-CH_2CH_2-C(H)(O)$               | C'   | -0.92918          | -0.92918          | 0                 | 0                 | -153.54487        | 0.91771         | 0.81549           | -16.68411              | -16.49325              | 65.99         | 114.01         | 30.58          | 1.76270   | 0.33183   |
| $C'-H$ (CH <sub>2</sub> ) (ii)    | C'   | -0.92918          | 0                 | 0                 | 0                 | -153.54487        | 0.91771         | 0.86359           | -15.75493              | -15.56407              | 77.49         | 102.51         | 41.48          | 1.23564   | 0.18708   |
| $C'-H$ (CH <sub>2</sub> ) (iii)   | C'   | -0.92918          | -0.92918          | 0                 | 0                 | -153.54487        | 0.91771         | 0.81549           | -16.68412              | -16.49325              | 68.47         | 111.53         | 35.84          | 1.35486   | 0.29933   |
| $C'-H$ (CH) (iii)                 | C'   | -0.92918          | -0.92918          | -0.92918          | 0                 | -154.40324        | 0.91771         | 0.77247           | -17.61330              | -17.42244              | 61.10         | 118.90         | 31.37          | 1.42988   | 0.37226   |
| $H_2C_2-C(H_2C_2O)-H$             | C'   | -0.92918          | 0                 | 0                 | 0                 | -152.54487        | 0.91771         | 0.86359           | -15.75493              | -15.56407              | 63.82         | 116.18         | 30.08          | 1.83879   | 0.38106   |
| $H_2C_2-C(H_2C_2O)-H$             | C'   | -0.92918          | -0.92918          | 0                 | 0                 | -153.47406        | 0.91771         | 0.81549           | -16.68412              | -16.49325              | 56.41         | 123.59         | 26.06          | 1.90890   | 0.45117   |
| $R-H_2C_2-C(H_2C_2O)-H$           | C'   | -0.92918          | -0.92918          | -0.92918          | 0                 | -154.40324        | 0.91771         | 0.77247           | -17.61330              | -17.42244              | 48.30         | 131.70         | 21.90          | 1.97162   | 0.51388   |
| $R-H_2C_2-C(H_2C_2O)-H$           | C'   | -0.92918          | -0.72457          | -0.72457          | -0.72457          | -154.71860        | 0.91771         | 0.75889           | -17.92866              | -17.73779              | 48.21         | 131.79         | 21.74          | 1.95734   | 0.50570   |
| $H_2C_2-C(H_2C_2O)-H$             | C'   | -0.92918          | -0.92918          | -0.92918          | 0                 | -154.40324        | 0.91771         | 0.77247           | -17.61330              | -17.42244              | 48.30         | 131.70         | 21.90          | 1.97162   | 0.51388   |
| $H_2C_2-C(H_2C_2O)-H$             | C'   | -0.92918          | -0.72457          | -0.72457          | -0.72457          | -154.51399        | 0.91771         | 0.76765           | -17.92866              | -17.73779              | 50.04         | 129.96         | 22.66          | 1.94462   | 0.49298   |
| $H_2C_2-C(H_2C_2O)-H$             | C'   | -0.92918          | -0.92918          | -0.92918          | 0                 | -154.40324        | 0.91771         | 0.77247           | -17.61330              | -17.42244              | 48.30         | 131.70         | 21.90          | 1.97162   | 0.51388   |
| $H_2C_2-C(H_2C_2O)-H$             | C'   | -0.92918          | -0.72457          | -0.72457          | -0.72457          | -154.51399        | 0.91771         | 0.76765           | -17.92866              | -17.73779              | 50.04         | 129.96         | 22.66          | 1.94462   | 0.49298   |
| $H_2C_2-C(H_2C_2O)-H$             | C'   | -0.92918          | -0.92918          | -0.92918          | 0                 | -154.40324        | 0.91771         | 0.77247           | -17.61330              | -17.42244              | 48.30         | 131.70         | 21.90          | 1.97162   | 0.51388   |
| $H_2C_2-C(H_2C_2O)-H$             | C'   | -0.92918          | -0.72457          | -0.72457          | -0.72457          | -154.51399        | 0.91771         | 0.76765           | -17.92866              | -17.73779              | 50.04         | 129.96         | 22.66          | 1.94462   | 0.49298   |

Table 15.90. The energy parameters (eV) of functional groups of alkyl aldehydes.

| Parameters                  | $CH_2$ (i) | $CH$ (i)  | $C=O$ Group | $C-C(OH)$ Group | $CH_3$ Group | $CH_2$ (ii) | $C-H$ (ii) | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) |
|-----------------------------|------------|-----------|-------------|-----------------|--------------|-------------|------------|-----------|-----------|-----------|-----------|-----------|-----------|
| $n_1$                       | 2          | 1         | 2           | 1               | 3            | 2           | 1          | 1         | 1         | 1         | 1         | 1         | 1         |
| $n_2$                       | 1          | 0         | 0           | 0               | 2            | 1           | 0          | 0         | 0         | 0         | 0         | 0         | 0         |
| $n_3$                       | 0          | 0         | 0           | 0               | 0            | 0           | 0          | 0         | 0         | 0         | 0         | 0         | 0         |
| $C_1$                       | 0.75       | 0.75      | 0.5         | 0.5             | 0.75         | 0.75        | 0.75       | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       |
| $C_2$                       | 1          | 1         | 1           | 1               | 1            | 1           | 1          | 1         | 1         | 1         | 1         | 1         | 1         |
| $C_3$                       | 1          | 1         | 1           | 1               | 1            | 1           | 1          | 1         | 1         | 1         | 1         | 1         | 1         |
| $C_4$                       | 0.91771    | 0.91771   | 0.85395     | 0.91771         | 0.91771      | 0.91771     | 0.91771    | 0.91771   | 0.91771   | 0.91771   | 0.91771   | 0.91771   | 0.91771   |
| $C_5$                       | 1          | 0         | 2           | 0               | 0            | 1           | 1          | 0         | 0         | 0         | 1         | 1         | 0         |
| $C_6$                       | 1          | 1         | 4           | 2               | 1            | 1           | 1          | 2         | 2         | 2         | 2         | 2         | 2         |
| $C_7$                       | 2          | 1         | 0           | 0               | 3            | 2           | 1          | 0         | 0         | 0         | 0         | 0         | 0         |
| $C_{10}$                    | 0.75       | 0.75      | 0.5         | 1               | 0.75         | 0.75        | 0.75       | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       |
| $C_{20}$                    | 1          | 1         | 1           | 1               | 1            | 1           | 1          | 1         | 1         | 1         | 1         | 1         | 1         |
| $V_e$ (eV)                  | -72.03287  | -35.12015 | -111.25473  | -30.19634       | -107.32728   | -70.41425   | -35.12015  | -28.79214 | -28.79214 | -28.79214 | -28.79214 | -28.79214 | -28.79214 |
| $V_p$ (eV)                  | 26.02344   | 12.87680  | 23.87467    | 9.50874         | 38.92728     | 25.78002    | 12.87680   | 9.33352   | 9.33352   | 9.33352   | 9.33352   | 9.33352   | 9.33352   |
| $T$ (eV)                    | 21.95990   | 10.48582  | 42.82081    | 7.37432         | 32.53914     | 21.06675    | 10.48582   | 6.77464   | 6.77464   | 6.77464   | 6.77464   | 6.77464   | 6.77464   |
| $V_e$ (eV)                  | -10.97995  | -5.24291  | -21.41040   | -3.68716        | -16.26957    | -10.53337   | -5.24291   | -3.38732  | -3.38732  | -3.38732  | -3.38732  | -3.38732  | -3.38732  |
| $E_{Lip}$ (eV)              | -14.63489  | -14.63489 | 0           | -14.63489       | -15.56407    | -15.56407   | -14.63489  | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 |
| $\Delta E_{Lip}$ (eV)       | 0          | 0         | -2.69893    | 0               | 0            | 0           | 0          | 0         | 0         | 0         | 0         | 0         | 0         |
| $E_{Lip}$ (eV)              | -14.63489  | -14.63489 | 2.69893     | -14.63489       | -15.56407    | -15.56407   | -14.63489  | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 |
| $E_{Lip}$ (eV)              | -49.66437  | -31.63533 | -63.27074   | -31.63534       | -67.69451    | -49.66493   | -31.63533  | -31.63537 | -31.63537 | -31.63537 | -31.63537 | -31.63537 | -31.63537 |
| $E_{Lip}$ (eV)              | 0          | 0         | -2.69893    | -1.85836        | 0            | 0           | 0          | -1.85836  | -1.85836  | -1.85836  | -1.85836  | -1.85836  | -1.85836  |
| $E_{Lip}$ (eV)              | -49.66493  | -31.63537 | -65.96966   | -33.49373       | -67.69450    | -49.66493   | -31.63537  | -33.49373 | -33.49373 | -33.49373 | -33.49373 | -33.49373 | -33.49373 |
| $\omega$ ( $10^{15}$ rad/s) | 25.2077    | 24.1759   | 59.4034     | 23.2291         | 24.9286      | 24.2751     | 24.1759    | 9.43699   | 9.43699   | 9.43699   | 9.43699   | 9.43699   | 9.43699   |
| $E_e$ (eV)                  | 16.59214   | 15.91299  | 39.10034    | 15.35563        | 16.40846     | 15.97831    | 15.91299   | 6.21159   | 6.21159   | 6.21159   | 6.21159   | 6.21159   | 6.21159   |
| $E_e$ (eV)                  | -0.23493   | -0.24966  | -0.40804    | -0.25966        | -0.25352     | -0.25017    | -0.24966   | -0.16515  | -0.16515  | -0.16515  | -0.16515  | -0.16515  | -0.16515  |
| $E_{K\alpha}$ (eV)          | 0.35352    | 0.35352   | 0.21077     | 0.13800         | 0.35352      | 0.35352     | 0.35352    | 0.12312   | 0.12312   | 0.12312   | 0.12312   | 0.12312   | 0.12312   |
| $E_{K\alpha}$ (eV)          | -0.07727   | -0.07200  | -0.30266    | -0.19066        | -0.22757     | -0.14502    | -0.07200   | -0.10359  | -0.10359  | -0.10359  | -0.10359  | -0.10359  | -0.10359  |
| $E_{K\alpha}$ (eV)          | 0.14803    | 0.14803   | 0.11441     | 0.14803         | 0.14803      | 0.14803     | 0.14803    | 0.14803   | 0.14803   | 0.14803   | 0.14803   | 0.14803   | 0.14803   |
| $E_{K\alpha}$ (eV)          | -49.81948  | -31.70737 | -66.57498   | -33.68439       | -67.92207    | -49.80996   | -31.70737  | -33.59732 | -33.59732 | -33.59732 | -33.59732 | -33.59732 | -33.59732 |
| $E_{K\alpha}$ (eV)          | -14.63489  | -14.63489 | -14.63489   | -14.63489       | -14.63489    | -14.63489   | -14.63489  | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{K\alpha}$ (eV)          | -13.59844  | -13.59844 | 0           | 0               | -13.59844    | -13.59844   | -13.59844  | 0         | 0         | 0         | 0         | 0         | 0         |
| $E_{K\alpha}$ (eV)          | 7.83968    | 3.47404   | 7.80660     | 4.41461         | 12.49186     | 7.83016     | 3.32601    | 4.32754   | 4.29921   | 4.29921   | 4.17951   | 3.97398   | 3.91734   |

Table 15.91. The total bond energies calculated using the functional group composition and the energies of Table 15.90 compared to the experimental values [3].

| Formula | $CH_2$ (i) | $CH$ (i) | $C=O$ Group | $C-C(OH)$ Group | $CH_3$ Group | $CH_2$ (ii) | $CH$ (ii) | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---------|------------|----------|-------------|-----------------|--------------|-------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------------------------------|-------------------------------------|----------------|
| $CH_2O$ | 1          | 0        | 1           | 0               | 0            | 0           | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 15.655                            | 15.655                              | 0.00056        |
| $CH_3O$ | 0          | 1        | 1           | 1               | 0            | 0           | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 28.18711                          | 28.198                              | 0.00039        |
| $CH_2O$ | 0          | 0        | 1           | 1               | 1            | 0           | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 40.34481                          | 40.345                              | 0.00000        |
| $CH_3O$ | 0          | 0        | 1           | 1               | 1            | 0           | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 52.50251                          | 52.491                              | -0.00022       |
| $CH_2O$ | 0          | 0        | 1           | 1               | 2            | 0           | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 52.60340                          | 52.604                              | 0.00001        |
| $CH_3O$ | 0          | 0        | 1           | 1               | 3            | 0           | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 64.66021                          | 64.682                              | 0.00034        |
| $CH_2O$ | 0          | 0        | 1           | 1               | 4            | 0           | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 88.97561                          | 88.942                              | -0.00038       |
| $CH_3O$ | 0          | 0        | 1           | 1               | 5            | 0           | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 101.1331                          | 101.179                             | 0.00045        |
| $CH_2O$ | 0          | 0        | 1           | 1               | 6            | 0           | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 101.2587                          | 101.259                             | 0.00053        |

Table 15.92. The bond angle parameters of alkyl aldehydes and experimental values [1]. In the calculation of  $\theta_i$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(atom - atom, mp^2, AO)$ .

| Atom of Angle                      | $2c_1$<br>Bond 1<br>( $\theta_1$ ) | $2c_2$<br>Bond 2<br>( $\theta_2$ ) | $2c'$<br>Terminal<br>Atom ( $\theta_3$ ) | $E_{\text{Terminal}}$<br>Atom 1<br>(Table 15.3.A) | Atom 1<br>Hybridization<br>Designation<br>(Table 15.3.A) | $E_{\text{Terminal}}$<br>Atom 2 | Atom 2<br>Hybridization<br>Designation<br>(Table 15.3.A) | $c_1$<br>Atom 1 | $c_2$<br>Atom 2<br>(Eq. 15.144) | $C_1$ | $C_2$ | $\phi_1$ | $\phi_2$ | $E_T$<br>(eV) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | Cal. $\theta$<br>( $^\circ$ ) | Exp. $\theta$<br>( $^\circ$ )                                 |
|------------------------------------|------------------------------------|------------------------------------|------------------------------------------|---------------------------------------------------|----------------------------------------------------------|---------------------------------|----------------------------------------------------------|-----------------|---------------------------------|-------|-------|----------|----------|---------------|----------------------------|----------------------------|-------------------------------|---------------------------------------------------------------|
| $\angle HC-H$<br>( $C-H_2(O)$ (i)) | 2.09132                            | 2.09132                            | 3.5637                                   | -16.39089                                         | 18                                                       | H                               | H                                                        | 0.83008         | 1                               | 1     | 1     | 0.75     | 1.20470  | 0             |                            |                            | 116.87                        | 116.5<br>(formaldehyde)                                       |
| $\angle C-C-H$<br>$RC(H)=O$        | 2.86175                            | 2.11323                            | 4.2269                                   | -15.75493                                         | 7                                                        | $C_b$                           | 1                                                        | 0.86359         | 0.91771                         | 0.75  | 1     | 0.75     | 1.06267  | 0             |                            |                            | 115.52                        | 115.3<br>(acetaldehyde)                                       |
| $\angle C-C-O$<br>Methane          | 2.86175                            | 2.79354                            | 4.5826                                   | -16.68412                                         | 25                                                       | $C_b$                           | 0                                                        | 0.81549         | 0.83295<br>(Eq. 15.144)         | 1     | 1     | 1        | 0.83472  | -1.65376      |                            |                            | 125.70                        | 124.1<br>(acetaldehyde)                                       |
| $\angle HC-H$                      | 2.11106                            | 2.11106                            | 3.4252                                   | -15.75493                                         | 7                                                        | H                               | H                                                        | 0.86359         | 1                               | 1     | 1     | 0.75     | 1.15796  | 0             |                            |                            | 108.44                        | 107<br>(propane)                                              |
| $\angle C-C-C$                     |                                    |                                    |                                          |                                                   |                                                          |                                 |                                                          |                 |                                 |       |       |          |          |               | 69.51                      |                            | 110.49                        | 112<br>(propane)<br>113.8<br>(butane)<br>110.8<br>(isobutane) |
| $\angle C-C-H$                     |                                    |                                    |                                          |                                                   |                                                          |                                 |                                                          |                 |                                 |       |       |          |          |               | 69.51                      |                            | 110.49                        | 111.0<br>(butane)<br>111.4<br>(isobutane)                     |
| Methyl<br>$\angle HC-H$            | 2.09711                            | 2.09711                            | 3.4252                                   | -15.75493                                         | 7                                                        | H                               | H                                                        | 0.86359         | 1                               | 1     | 1     | 0.75     | 1.15796  | 0             |                            |                            | 109.50                        | 109.8<br>(acetaldehyde)                                       |
| $\angle C-C-C$                     |                                    |                                    |                                          |                                                   |                                                          |                                 |                                                          |                 |                                 |       |       |          |          |               | 70.56                      |                            | 109.44                        |                                                               |
| $\angle C-C-H$                     |                                    |                                    |                                          |                                                   |                                                          |                                 |                                                          |                 |                                 |       |       |          |          |               | 70.56                      |                            | 109.44                        |                                                               |
| $\angle C-C-C$<br>iso $C_a$        | 2.91547                            | 2.91547                            | 4.7958                                   | -16.68412                                         | 25                                                       | $C_b$                           | 25                                                       | 0.81549         | 0.81549                         | 1     | 1     | 1        | 0.81549  | -1.83836      |                            |                            | 110.67                        | 110.8<br>(isobutane)                                          |
| $\angle C-C-H$<br>iso $C_a$        | 2.91547                            | 2.11323                            | 4.1633                                   | -15.55033                                         | 5                                                        | $C_b$                           | 1                                                        | 0.87495         | 0.91771                         | 0.75  | 1     | 0.75     | 1.04887  | 0             |                            |                            | 110.76                        |                                                               |
| $\angle C-C-H$<br>iso $C_a$        | 2.91547                            | 2.09711                            | 4.1633                                   | -15.55033                                         | 3                                                        | $C_b$                           | 1                                                        | 0.87495         | 0.91771                         | 0.75  | 1     | 0.75     | 1.04887  | 0             |                            |                            | 111.27                        | 111.4<br>(isobutane)                                          |
| $\angle C-C-C$<br>tert $C_a$       | 2.90327                            | 2.90327                            | 4.7958                                   | -15.55033                                         | 5                                                        | $C_b$                           | 1                                                        | 0.87495         | 0.91771                         | 0.75  | 1     | 0.75     | 1.04887  | -1.83836      |                            |                            | 111.27                        | 111.4<br>(isobutane)                                          |
| $\angle C-C-C$                     |                                    |                                    |                                          |                                                   |                                                          |                                 |                                                          |                 |                                 |       |       |          |          |               | 72.50                      |                            | 107.50                        |                                                               |

KETONES ( $C_nH_{2n}O$ ,  $n = 1, 2, 3, 4, 5 \dots \infty$ )

The alkyl ketones,  $C_nH_{2n}O$ , each have a  $C=O$  moiety that comprises a functional group. Each of the two single bonds of carbon to the carbonyl carbon atom,  $C-C(O)$ , is also a functional group. The alkyl portion of the alkyl ketone may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in ketones are equivalent to those in branched-chain alkanes.

The  $C=O$  and  $C-C(O)$  groups are solved by hybridizing the  $2s$  and  $2p$  AOs of each  $C$  atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the  $O$  AO or between two  $C2sp^3$  HOs, respectively, to form a MO permits each participating orbital to decrease in radius and energy. In alkyl ketones, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)) and the  $O$  AO has an energy of  $E(O) = -13.61806 \text{ eV}$ . To meet the equipotential condition of the union of the  $C=O$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the  $C=O$ -bond MO given by Eq. (15.114) is  $c_2(C2sp^3HO \text{ to } O) = 0.85395$ . The unpaired electrons created by bond breakage of the double  $C=O$  bond requires that two times the  $O2p$  AO magnetic energy  $E_{mag}$  (Eq. (15.60)) be subtracted from the total energy to give  $E_D(\text{Group}) \text{ (eV)}$  for  $C=O$ .

As in the case with aldehydes,  $E_T(\text{atom-atom}, msp^3.AO)$  of the  $C=O$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $O$  atoms to the MO is  $-2.69893 \text{ eV}$  which is an energy minimum for the double bond between the pair of  $C2sp^3$  HO electrons of the  $C$  atom and the pair of AO electrons of the  $O$  atom. It is given as a linear combination of



the energy contributions corresponding to a double bond,  $-1.13379 \text{ eV}$  (Eq. (14.247)), and a triple bond,  $-1.56513 \text{ eV}$  (Eq. (14.342)). The triple bond contribution includes the  $C2sp^3$  HO electron of the  $C-C(O)$  bond in addition to the pair involved directly in the double bond with  $O$ . Consequently,  $E_T(\text{atom-atom}, msp^3.AO)$  of the  $C-C(O)$ -bond MO is  $-1.44915 \text{ eV}$ ,  
 5 corresponding to the energy contributions of the two  $C2sp^3$  HOs to the single bond that are equivalent to those of methyl groups,  $-0.72457 \text{ eV}$  (Eq. (14.151)). Since there are two  $C-C(O)$  bonds in ketones versus one in aldehydes,  $C_{1o} = C_1$  in Eq. (15.52) for each  $C-C(O)$  ketone bond.

The symbols of the functional groups of alkyl ketones are given in Table 15.93. The  
 10 geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.55)) parameters of alkyl ketones are given in Tables 15.94, 15.95, and 15.96, respectively. The total energy of each alkyl ketone given in Table 15.97 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.96 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by  
 15 bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_D(\text{Group})$  ( $\text{eV}$ ) values based on composition is given by Eq. (15.58). The bond angle parameters of alkyl ketones determined using Eqs. (15.79-15.108) are given in Table 15.98.

Table 15.93. The symbols of functional groups of alkyl ketones.

| Functional Group  | Group Symbol |
|-------------------|--------------|
| $C=O$             | $C=O$        |
| $C-C(O)$          | $C-C(O)$     |
| $CH_3$ group      | $C-H (CH_3)$ |
| $CH_2$ group      | $C-H (CH_2)$ |
| $CH$              | $C-H$        |
| CC bond (n-C)     | $C-C$ (a)    |
| CC bond (iso-C)   | $C-C$ (b)    |
| CC bond (tert-C)  | $C-C$ (c)    |
| CC (iso to iso-C) | $C-C$ (d)    |
| CC (t to t-C)     | $C-C$ (e)    |
| CC (t to iso-C)   | $C-C$ (f)    |

Table 15.94. The geometrical bond parameters of alkyl ketones and experimental values [1].

| Parameter                | C=O<br>Group                                | C-C(O)<br>Group                             | C-H (CH <sub>3</sub> )<br>Group                 | C-H (CH <sub>2</sub> )<br>Group                 | C-H<br>Group         | C-C (a)<br>Group                        | C-C (b)<br>Group                        | C-C (c)<br>Group                        | C-C (d)<br>Group                        | C-C (e)<br>Group                        | C-C (f)<br>Group                        |
|--------------------------|---------------------------------------------|---------------------------------------------|-------------------------------------------------|-------------------------------------------------|----------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|
| $a$ (a <sub>0</sub> )    | 1.312172                                    | 2.04740                                     | 1.64920                                         | 1.67122                                         | 1.67465              | 2.12499                                 | 2.12499                                 | 2.10725                                 | 2.12499                                 | 2.10725                                 | 2.10725                                 |
| $c'$ (a <sub>0</sub> )   | 1.14550                                     | 1.43087                                     | 1.04856                                         | 1.05553                                         | 1.05661              | 1.45744                                 | 1.45744                                 | 1.45164                                 | 1.45744                                 | 1.45164                                 | 1.45164                                 |
| Bond Length<br>2c' (Å)   | 1.21235                                     | 1.51437                                     | 1.10974                                         | 1.11713                                         | 1.11827              | 1.54280                                 | 1.54280                                 | 1.53635                                 | 1.54280                                 | 1.53635                                 | 1.53635                                 |
| Exp. Bond Length<br>(Å)  | 1.213<br>(acetone)<br>1.219<br>(2-butanone) | 1.520<br>(acetone)<br>1.518<br>(2-butanone) | 1.107<br>(C-H propane)<br>1.117<br>(C-H butane) | 1.107<br>(C-H propane)<br>1.117<br>(C-H butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $h, c$ (a <sub>0</sub> ) | 0.64002                                     | 1.46439                                     | 1.27295                                         | 1.29569                                         | 1.29924              | 1.54616                                 | 1.54616                                 | 1.52750                                 | 1.54616                                 | 1.52750                                 | 1.52750                                 |
| $u$                      | 0.87298                                     | 0.69887                                     | 0.63580                                         | 0.63159                                         | 0.63095              | 0.68600                                 | 0.68600                                 | 0.68888                                 | 0.68600                                 | 0.68888                                 | 0.68888                                 |

Table 15.95. The MO to HO intercept geometrical bond parameters of alkyl ketones.  $R, R', R''$  are H or alkyl groups.  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{msp}, \text{AO})$ .

| Bond                        | Atom           | $E_r$<br>(eV)<br>Bond 1 | $E_r$<br>(eV)<br>Bond 2 | $E_r$<br>(eV)<br>Bond 3 | $E_r$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>C2sp <sup>3</sup><br>(eV) | $r_{\text{final}}$<br>(a <sub>0</sub> ) | $r_{\text{final}}$<br>(a <sub>0</sub> ) | $E_{\text{C2sp}^3}$<br>(eV)<br>Final | $\theta$<br>(°) | $\theta_1$<br>(°) | $\theta_2$<br>(°) | $d_1$<br>(a <sub>0</sub> ) | $d_2$<br>(a <sub>0</sub> ) |
|-----------------------------|----------------|-------------------------|-------------------------|-------------------------|-------------------------|----------------------------------------------------|-----------------------------------------|-----------------------------------------|--------------------------------------|-----------------|-------------------|-------------------|----------------------------|----------------------------|
| $R'C_1H_3(RC_2H_2C_3=O)$    | O              | -1.34946                | 0                       | 0                       | 0                       | -154.41430                                         | 0.91771                                 | 0.84115                                 | -16.17521                            | 136.09          | 43.91             | 65.72             | 0.33955                    | 0.60595                    |
| $R'C_1H_3(RC_2H_2C_3=O)$    | C <sub>1</sub> | -1.34946                | -0.72458                | -0.72458                | 0                       | -152.40266                                         | 0.91771                                 | 0.77199                                 | -17.62437                            | 133.02          | 46.98             | 61.86             | 0.61878                    | 0.52672                    |
| $H_2C_2-C_1(O)(R')$         | C <sub>1</sub> | -0.72458                | 0                       | 0                       | 0                       | -153.26945                                         | 0.91771                                 | 0.87495                                 | -15.55033                            | 73.62           | 106.38            | 34.98             | 1.67762                    | 0.246675                   |
| $RH_2C_1-H_2C_2-C_1(O)(R')$ | C <sub>1</sub> | -0.72458                | -0.92918                | 0                       | 0                       | -152.54487                                         | 0.91771                                 | 0.86359                                 | -16.47951                            | 67.40           | 112.60            | 31.26             | 1.74821                    | 0.31734                    |
| $C'-H(CH_3)$                | C'             | -0.92918                | 0                       | 0                       | 0                       | -153.47066                                         | 0.91771                                 | 0.81549                                 | -15.75493                            | 77.49           | 102.51            | 41.48             | 1.23564                    | 0.18708                    |
| $C'-H(CH_2)$                | C'             | -0.92918                | -0.92918                | 0                       | 0                       | -153.47066                                         | 0.91771                                 | 0.81549                                 | -16.68412                            | 68.47           | 111.53            | 35.84             | 1.35486                    | 0.29933                    |
| $H_2C_2-C_1(H_2C_2-)$       | C'             | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                         | 0.91771                                 | 0.77247                                 | -17.61330                            | 61.10           | 118.90            | 31.37             | 1.42988                    | 0.37326                    |
| $H_2C_2-C_1(H_2C_2-)$       | C <sub>1</sub> | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                         | 0.91771                                 | 0.86359                                 | -15.75493                            | 63.82           | 116.18            | 30.08             | 1.83879                    | 0.38106                    |
| $H_2C_2-C_1(H_2C_2-)$       | C <sub>1</sub> | -0.92918                | -0.92918                | 0                       | 0                       | -153.47066                                         | 0.91771                                 | 0.81549                                 | -16.68412                            | 56.41           | 123.59            | 26.06             | 1.90890                    | 0.45117                    |
| $R-H_2C_2-C_1(H_2C_2-)$     | C <sub>1</sub> | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                         | 0.91771                                 | 0.77247                                 | -17.61330                            | 48.30           | 131.70            | 21.90             | 1.97162                    | 0.51388                    |
| $R-H_2C_2-C_1(H_2C_2-)$     | C <sub>1</sub> | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -154.71860                                         | 0.91771                                 | 0.75889                                 | -17.92856                            | 48.21           | 131.79            | 21.74             | 1.95734                    | 0.50570                    |
| $R-H_2C_2-C_1(H_2C_2-)$     | C <sub>1</sub> | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                         | 0.91771                                 | 0.77247                                 | -17.61330                            | 48.30           | 131.70            | 21.90             | 1.97162                    | 0.51388                    |
| $R-H_2C_2-C_1(H_2C_2-)$     | C <sub>1</sub> | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -154.51399                                         | 0.91771                                 | 0.76765                                 | -17.92856                            | 50.04           | 129.96            | 22.66             | 1.94462                    | 0.49298                    |
| $R-H_2C_2-C_1(H_2C_2-)$     | C <sub>1</sub> | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                         | 0.91771                                 | 0.77247                                 | -17.61330                            | 48.30           | 131.70            | 21.90             | 1.97162                    | 0.51388                    |
| $R-H_2C_2-C_1(H_2C_2-)$     | C <sub>1</sub> | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -154.51399                                         | 0.91771                                 | 0.76765                                 | -17.92856                            | 50.04           | 129.96            | 22.66             | 1.94462                    | 0.49298                    |
| $R-H_2C_2-C_1(H_2C_2-)$     | C <sub>1</sub> | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                         | 0.91771                                 | 0.77247                                 | -17.61330                            | 48.30           | 131.70            | 21.90             | 1.97162                    | 0.51388                    |
| $R-H_2C_2-C_1(H_2C_2-)$     | C <sub>1</sub> | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -154.51399                                         | 0.91771                                 | 0.76765                                 | -17.92856                            | 50.04           | 129.96            | 22.66             | 1.94462                    | 0.49298                    |

Table 15.96. The energy parameters (eV) of functional groups of alkyl ketones.

| Parameters                                                   | C=O<br>Group | C-C(O)<br>Group | CH <sub>3</sub><br>Group | CH <sub>2</sub><br>Group | C-H<br>Group   | C-C (a)<br>Group | C-C (b)<br>Group | C-C (c)<br>Group | C-C (d)<br>Group | C-C (e)<br>Group | C-C (f)<br>Group |
|--------------------------------------------------------------|--------------|-----------------|--------------------------|--------------------------|----------------|------------------|------------------|------------------|------------------|------------------|------------------|
| $\eta_1$                                                     | 2            | 1               | 3                        | 2                        | 1              | 1                | 1                | 1                | 1                | 1                | 1                |
| $\eta_2$                                                     | 0            | 0               | 2                        | 1                        | 0              | 0                | 0                | 0                | 0                | 0                | 0                |
| $\eta_3$                                                     | 0            | 0               | 0                        | 0                        | 0              | 0                | 0                | 0                | 0                | 0                | 0                |
| $\eta_4$                                                     | 0.5          | 0.5             | 0.75                     | 0.75                     | 0.75           | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              |
| $\zeta_1$                                                    | 1            | 1               | 1                        | 1                        | 1              | 1                | 1                | 1                | 1                | 1                | 1                |
| $\zeta_2$                                                    | 1            | 1               | 1                        | 1                        | 1              | 1                | 1                | 1                | 1                | 1                | 1                |
| $\zeta_3$                                                    | 0.85395      | 0.91771         | 0.91771                  | 0.91771                  | 0.91771        | 0.91771          | 0.91771          | 0.91771          | 0.91771          | 0.91771          | 0.91771          |
| $\zeta_4$                                                    | 2            | 0               | 0                        | 1                        | 1              | 0                | 0                | 0                | 1                | 1                | 0                |
| $\zeta_5$                                                    | 4            | 2               | 1                        | 1                        | 1              | 2                | 2                | 2                | 2                | 2                | 2                |
| $\zeta_6$                                                    | 0            | 0               | 3                        | 2                        | 1              | 0                | 0                | 0                | 0                | 0                | 0                |
| $\zeta_{in}$                                                 | 0.5          | 1               | 0.75                     | 0.75                     | 0.75           | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              |
| $\zeta_{3a}$                                                 | 1            | 1               | 1                        | 1                        | 1              | 1                | 1                | 1                | 1                | 1                | 1                |
| $V_e$ (eV)                                                   | -109.17602   | -30.19634       | -107.32728               | -70.41425                | -35.12015      | -28.79214        | -28.79214        | -29.10112        | -28.79214        | -29.10112        | -29.10112        |
| $V_p$ (eV)                                                   | 23.75521     | 9.50874         | 38.92728                 | 25.78002                 | 12.87680       | 9.33352          | 9.33352          | 9.37273          | 9.33352          | 9.37273          | 9.37273          |
| $T$ (eV)                                                     | 41.60126     | 7.37432         | 32.53914                 | 21.06675                 | 10.48582       | 6.77464          | 6.77464          | 6.90500          | 6.77464          | 6.90500          | 6.90500          |
| $V_n$ (eV)                                                   | -20.80063    | -3.68716        | -16.26937                | -10.53337                | -5.24291       | -3.38732         | -3.38732         | -3.45250         | -3.38732         | -3.45250         | -3.45250         |
| $E(x \text{ in})$ (eV)                                       | 0            | -14.63489       | -15.56407                | -15.56407                | -14.63489      | -15.56407        | -15.56407        | -15.35946        | -15.56407        | -15.35946        | -15.35946        |
| $\Delta E_{H_{2,30}}$ (eV)                                   | -1.34946     | 0               | 0                        | 0                        | 0              | 0                | 0                | 0                | 0                | 0                | 0                |
| $E_T$ (eV)                                                   | 1.34946      | -14.63489       | -15.56407                | -15.56407                | -14.63489      | -15.56407        | -15.56407        | -15.35946        | -15.56407        | -15.35946        | -15.35946        |
| $E_T(x \text{ in})$ (eV)                                     | -63.27071    | -31.63534       | -67.69451                | -49.66493                | -31.63533      | -31.63537        | -31.63537        | -31.63535        | -31.63537        | -31.63535        | -31.63535        |
| $E_T(\text{atom} - \text{atom}, \text{msq}, \text{AO})$ (eV) | -2.69893     | -1.44915        | 0                        | 0                        | 0              | -1.85836         | -1.85836         | -1.44915         | -1.85836         | -1.44915         | -1.44915         |
| $E_T(x \text{ in})$ (eV)                                     | -65.96966    | -33.08452       | -67.69450                | -49.66493                | -31.63537      | -33.49373        | -33.49373        | -33.08452        | -33.49373        | -33.08452        | -33.08452        |
| $\omega$ ( $10^6 \text{ rad/s}$ )                            | 57.0928      | 16.4962         | 24.9286                  | 24.2751                  | 24.1759        | 9.43699          | 9.43699          | 15.4846          | 9.43699          | 9.55643          | 9.55643          |
| $E_K$ (eV)                                                   | 37.57947     | 10.83807        | 16.40846                 | 15.97831                 | 15.91299       | 6.21159          | 6.21159          | 10.19220         | 6.21159          | 6.29021          | 6.29021          |
| $E_p$ (eV)                                                   | -0.40003     | -0.21568        | -0.25352                 | -0.25017                 | -0.24966       | -0.16515         | -0.16515         | -0.20896         | -0.16515         | -0.16416         | -0.16416         |
| $E_{Kw}$ (eV)                                                | 0.21462      | 0.14655         | 0.35532                  | 0.35532                  | 0.35532        | 0.12312          | 0.12312          | 0.09944          | 0.12312          | 0.12312          | 0.12312          |
| $E_{Kw}$ (eV)                                                | [27]         | [28]            | (Eq. (13.458))           | (Eq. (13.458))           | (Eq. (13.458)) | [2]              | [4]              | [5]              | [2]              | [2]              | [2]              |
| $E_{Kw}$ (eV)                                                | -0.29272     | -0.14240        | -0.22757                 | -0.14502                 | -0.07200       | -0.10359         | -0.07526         | -0.15924         | -0.10359         | -0.10260         | -0.10260         |
| $E_{Kw}$ (eV)                                                | 0.11441      | 0.14803         | 0.14803                  | 0.14803                  | 0.14803        | 0.14803          | 0.14803          | 0.14803          | 0.14803          | 0.14803          | 0.14803          |
| $E_T(x \text{ in})$ (eV)                                     | -66.55510    | -33.22692       | -67.92207                | -49.80996                | -31.70737      | -33.59732        | -33.59732        | -33.24376        | -33.59732        | -33.18712        | -33.18712        |
| $E_{Kw}(x \text{ in})$ (eV)                                  | -14.63489    | -14.63489       | -14.63489                | -14.63489                | -14.63489      | -14.63489        | -14.63489        | -14.63489        | -14.63489        | -14.63489        | -14.63489        |
| $E_{Kw}(x \text{ in})$ (eV)                                  | 0            | 0               | -13.59844                | -13.59844                | -13.59844      | 0                | 0                | 0                | 0                | 0                | 0                |
| $E_{Kw}(x \text{ in})$ (eV)                                  | 7.78672      | 3.95714         | 12.49186                 | 7.83016                  | 3.32601        | 4.32754          | 4.29921          | 3.97398          | 4.17951          | 3.62128          | 3.91734          |

Table 15.97. The total bond energies of alkyl ketones calculated using the functional group composition and the energies of Table 15.96 compared to the experimental values [3]. The magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_b$  ( $eV$ ) values based on composition is given by (15.57).

| Formula                            | Name             | C=O Group | C-C(O) Group | C <sub>1</sub> H <sub>3</sub> | C <sub>1</sub> H <sub>2</sub> | CH | C-C (a) | C-C (b) | C-C (c) | C-C (d) | C-C (e) | C-C (f) | E <sub>mag</sub> | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|------------------------------------|------------------|-----------|--------------|-------------------------------|-------------------------------|----|---------|---------|---------|---------|---------|---------|------------------|-----------------------------------|-------------------------------------|----------------|
| C <sub>2</sub> H <sub>4</sub> O    | Acetone          | 1         | 2            | 2                             | 0                             | 0  | 0       | 0       | 0       | 0       | 0       | 0       | 0                | 40.672                            | 40.672                              | -0.00031       |
| C <sub>3</sub> H <sub>6</sub> O    | 2-Butanone       | 1         | 2            | 2                             | 1                             | 0  | 1       | 0       | 0       | 0       | 0       | 0       | 0                | 52.842                            | 52.84                               | -0.00005       |
| C <sub>4</sub> H <sub>8</sub> O    | 3-Pentanone      | 1         | 2            | 2                             | 2                             | 0  | 2       | 0       | 0       | 0       | 0       | 0       | 0                | 65.00012                          | 64.997                              | -0.00005       |
| C <sub>5</sub> H <sub>10</sub> O   | 4-Hexanone       | 1         | 2            | 2                             | 2                             | 0  | 2       | 0       | 0       | 0       | 0       | 0       | 0                | 77.15782                          | 77.152                              | -0.00059       |
| C <sub>6</sub> H <sub>12</sub> O   | 5-Heptanone      | 1         | 2            | 2                             | 2                             | 0  | 3       | 0       | 0       | 0       | 0       | 0       | 0                | 89.31552                          | 89.306                              | -0.00088       |
| C <sub>7</sub> H <sub>14</sub> O   | 6-Octanone       | 1         | 2            | 2                             | 3                             | 0  | 3       | 0       | 0       | 0       | 0       | 0       | 0                | 101.47106                         | 101.460                             | -0.00093       |
| C <sub>8</sub> H <sub>16</sub> O   | 7-Nonanone       | 1         | 2            | 2                             | 3                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 113.63092                         | 113.632                             | 0.00001        |
| C <sub>9</sub> H <sub>18</sub> O   | 8-Decanone       | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 125.78764                         | 125.787                             | 0.00000        |
| C <sub>10</sub> H <sub>20</sub> O  | 9-Undecanone     | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 137.94432                         | 137.944                             | 0.00000        |
| C <sub>11</sub> H <sub>22</sub> O  | 10-Dodecanone    | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 150.10101                         | 150.101                             | 0.00000        |
| C <sub>12</sub> H <sub>24</sub> O  | 11-Tridecanone   | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 162.25771                         | 162.257                             | 0.00000        |
| C <sub>13</sub> H <sub>26</sub> O  | 12-Tetradecanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 174.41482                         | 174.414                             | 0.00000        |
| C <sub>14</sub> H <sub>28</sub> O  | 13-Pentadecanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 186.57193                         | 186.571                             | 0.00000        |
| C <sub>15</sub> H <sub>30</sub> O  | 14-Hexadecanone  | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 198.72904                         | 198.729                             | 0.00000        |
| C <sub>16</sub> H <sub>32</sub> O  | 15-Heptadecanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 210.88615                         | 210.886                             | 0.00000        |
| C <sub>17</sub> H <sub>34</sub> O  | 16-Octadecanone  | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 223.04326                         | 223.043                             | 0.00000        |
| C <sub>18</sub> H <sub>36</sub> O  | 17-Nonadecanone  | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 235.20037                         | 235.200                             | 0.00000        |
| C <sub>19</sub> H <sub>38</sub> O  | 18-Docosanone    | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 247.35748                         | 247.357                             | 0.00000        |
| C <sub>20</sub> H <sub>40</sub> O  | 19-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 259.51459                         | 259.514                             | 0.00000        |
| C <sub>21</sub> H <sub>42</sub> O  | 20-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 271.67170                         | 271.671                             | 0.00000        |
| C <sub>22</sub> H <sub>44</sub> O  | 21-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 283.82881                         | 283.828                             | 0.00000        |
| C <sub>23</sub> H <sub>46</sub> O  | 22-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 295.98592                         | 295.985                             | 0.00000        |
| C <sub>24</sub> H <sub>48</sub> O  | 23-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 308.14303                         | 308.143                             | 0.00000        |
| C <sub>25</sub> H <sub>50</sub> O  | 24-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 320.29914                         | 320.299                             | 0.00000        |
| C <sub>26</sub> H <sub>52</sub> O  | 25-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 332.45625                         | 332.456                             | 0.00000        |
| C <sub>27</sub> H <sub>54</sub> O  | 26-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 344.61336                         | 344.613                             | 0.00000        |
| C <sub>28</sub> H <sub>56</sub> O  | 27-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 356.77047                         | 356.770                             | 0.00000        |
| C <sub>29</sub> H <sub>58</sub> O  | 28-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 368.92758                         | 368.927                             | 0.00000        |
| C <sub>30</sub> H <sub>60</sub> O  | 29-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 381.08469                         | 381.084                             | 0.00000        |
| C <sub>31</sub> H <sub>62</sub> O  | 30-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 393.24180                         | 393.241                             | 0.00000        |
| C <sub>32</sub> H <sub>64</sub> O  | 31-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 405.39891                         | 405.398                             | 0.00000        |
| C <sub>33</sub> H <sub>66</sub> O  | 32-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 417.55602                         | 417.556                             | 0.00000        |
| C <sub>34</sub> H <sub>68</sub> O  | 33-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 429.71313                         | 429.713                             | 0.00000        |
| C <sub>35</sub> H <sub>70</sub> O  | 34-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 441.87024                         | 441.870                             | 0.00000        |
| C <sub>36</sub> H <sub>72</sub> O  | 35-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 454.02735                         | 454.027                             | 0.00000        |
| C <sub>37</sub> H <sub>74</sub> O  | 36-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 466.18446                         | 466.184                             | 0.00000        |
| C <sub>38</sub> H <sub>76</sub> O  | 37-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 478.34157                         | 478.341                             | 0.00000        |
| C <sub>39</sub> H <sub>78</sub> O  | 38-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 490.49868                         | 490.498                             | 0.00000        |
| C <sub>40</sub> H <sub>80</sub> O  | 39-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 502.65579                         | 502.655                             | 0.00000        |
| C <sub>41</sub> H <sub>82</sub> O  | 40-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 514.81290                         | 514.812                             | 0.00000        |
| C <sub>42</sub> H <sub>84</sub> O  | 41-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 526.97001                         | 526.970                             | 0.00000        |
| C <sub>43</sub> H <sub>86</sub> O  | 42-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 539.12712                         | 539.127                             | 0.00000        |
| C <sub>44</sub> H <sub>88</sub> O  | 43-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 551.28423                         | 551.284                             | 0.00000        |
| C <sub>45</sub> H <sub>90</sub> O  | 44-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 563.44134                         | 563.441                             | 0.00000        |
| C <sub>46</sub> H <sub>92</sub> O  | 45-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 575.59845                         | 575.598                             | 0.00000        |
| C <sub>47</sub> H <sub>94</sub> O  | 46-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 587.75556                         | 587.755                             | 0.00000        |
| C <sub>48</sub> H <sub>96</sub> O  | 47-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 599.91267                         | 599.912                             | 0.00000        |
| C <sub>49</sub> H <sub>98</sub> O  | 48-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 612.06978                         | 612.069                             | 0.00000        |
| C <sub>50</sub> H <sub>100</sub> O | 49-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 624.22689                         | 624.226                             | 0.00000        |
| C <sub>51</sub> H <sub>102</sub> O | 50-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 636.38400                         | 636.384                             | 0.00000        |
| C <sub>52</sub> H <sub>104</sub> O | 51-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 648.54111                         | 648.541                             | 0.00000        |
| C <sub>53</sub> H <sub>106</sub> O | 52-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 660.69822                         | 660.698                             | 0.00000        |
| C <sub>54</sub> H <sub>108</sub> O | 53-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 672.85533                         | 672.855                             | 0.00000        |
| C <sub>55</sub> H <sub>110</sub> O | 54-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 685.01244                         | 685.012                             | 0.00000        |
| C <sub>56</sub> H <sub>112</sub> O | 55-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 697.16955                         | 697.169                             | 0.00000        |
| C <sub>57</sub> H <sub>114</sub> O | 56-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 709.32666                         | 709.326                             | 0.00000        |
| C <sub>58</sub> H <sub>116</sub> O | 57-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 721.48377                         | 721.483                             | 0.00000        |
| C <sub>59</sub> H <sub>118</sub> O | 58-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 733.64088                         | 733.640                             | 0.00000        |
| C <sub>60</sub> H <sub>120</sub> O | 59-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 745.79799                         | 745.797                             | 0.00000        |
| C <sub>61</sub> H <sub>122</sub> O | 60-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 757.95510                         | 757.955                             | 0.00000        |
| C <sub>62</sub> H <sub>124</sub> O | 61-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 770.11221                         | 770.112                             | 0.00000        |
| C <sub>63</sub> H <sub>126</sub> O | 62-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 782.26932                         | 782.269                             | 0.00000        |
| C <sub>64</sub> H <sub>128</sub> O | 63-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 794.42643                         | 794.426                             | 0.00000        |
| C <sub>65</sub> H <sub>130</sub> O | 64-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 806.58354                         | 806.583                             | 0.00000        |
| C <sub>66</sub> H <sub>132</sub> O | 65-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 818.74065                         | 818.740                             | 0.00000        |
| C <sub>67</sub> H <sub>134</sub> O | 66-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 830.89776                         | 830.897                             | 0.00000        |
| C <sub>68</sub> H <sub>136</sub> O | 67-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 843.05487                         | 843.054                             | 0.00000        |
| C <sub>69</sub> H <sub>138</sub> O | 68-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 855.21198                         | 855.211                             | 0.00000        |
| C <sub>70</sub> H <sub>140</sub> O | 69-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 867.36909                         | 867.369                             | 0.00000        |
| C <sub>71</sub> H <sub>142</sub> O | 70-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 879.52620                         | 879.526                             | 0.00000        |
| C <sub>72</sub> H <sub>144</sub> O | 71-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 891.68331                         | 891.683                             | 0.00000        |
| C <sub>73</sub> H <sub>146</sub> O | 72-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 903.84042                         | 903.840                             | 0.00000        |
| C <sub>74</sub> H <sub>148</sub> O | 73-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 915.99753                         | 915.997                             | 0.00000        |
| C <sub>75</sub> H <sub>150</sub> O | 74-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 928.15464                         | 928.154                             | 0.00000        |
| C <sub>76</sub> H <sub>152</sub> O | 75-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 940.31175                         | 940.311                             | 0.00000        |
| C <sub>77</sub> H <sub>154</sub> O | 76-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 952.46886                         | 952.468                             | 0.00000        |
| C <sub>78</sub> H <sub>156</sub> O | 77-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 964.62597                         | 964.625                             | 0.00000        |
| C <sub>79</sub> H <sub>158</sub> O | 78-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 976.78308                         | 976.783                             | 0.00000        |
| C <sub>80</sub> H <sub>160</sub> O | 79-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 988.94019                         | 988.940                             | 0.00000        |
| C <sub>81</sub> H <sub>162</sub> O | 80-Triacontanone | 1         | 2            | 2                             | 4                             | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 1001.09730                        | 1001.097                            | 0.00000        |
| C <sub>82</sub> H <sub>164</sub> O | 81-Tria          |           |              |                               |                               |    |         |         |         |         |         |         |                  |                                   |                                     |                |

# CARBOXYLIC ACIDS ( $C_nH_{2n}O_2$ , $n = 1, 2, 3, 4, 5 \dots \infty$ )

The alkyl carboxylic acids,  $C_nH_{2n}O_2$ , comprise a  $C=O$  functional group, and the single bond of carbon to the carbonyl carbon atom,  $C-C(O)$ , is also a functional group. Formic acid has a  $HC=O$  moiety that comprises a more stable  $C=O$  functional group and a  $CH$  functional group. All carboxylic acids further comprise a  $C-OH$  moiety that comprises  $C-O$  and  $OH$  functional groups. The alkyl portion of the alkyl carboxylic acid may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acids are equivalent to those in branched-chain alkanes.

The  $CH$  functional group was solved in the Hydrogen Carbide ( $CH$ ) section except that the energy of the  $C-H$  MO is matched to the carbon-atom contribution to  $\Delta E_{H_2MO}(AO/HO)$  and  $E_T(atom-atom,msp^3.AO)$  of the  $C-O$  group. The alkyl carboxylic acid  $C=O$  and  $C-C(O)$  groups are equivalent to those given in the Aldehydes section except that  $\bar{E}_{Kvib}$  is that of a carboxylic acid. The formic acid  $C=O$  group is solved equivalently to that of the alkyl carboxylic acid group, except that  $\Delta E_{H_2MO}(AO/HO)$  and  $E_T(atom-atom,msp^3.AO)$  correspond to a 25% increase in the donation of charge density from the orbitals of the atoms to the  $C=O$  MO due to the presence of a  $H$  bound to the carbonyl carbon. Also,  $\bar{E}_{Kvib}$  is that corresponding to formic acid. The  $C-O$  and  $OH$  groups are equivalent to those of alkyl alcohols given in the corresponding section except that the energy of the  $C-O$  MO is matched to that of the  $C=O$  group and  $\bar{E}_{Kvib}$  is that of a carboxylic acid.  $\Delta E_{H_2MO}(AO/HO)$  of the  $C-O$  group is equal to  $E_T(atom-atom,msp^3.AO)$  of the alkyl  $C=O$  group in order to match the energies of the corresponding MOs.

As in the case with aldehydes and ketones,  $E_T(atom-atom,msp^3.AO)$  of the  $C=O$ -bond MO in Eq. (15.52) of alkyl carboxylic acids due to the charge donation from the  $C$  and  $O$

atoms to the MO is  $-2.69893 \text{ eV}$  which is an energy minimum for the double bond between the pair of  $C2sp^3$  HO electrons of the  $C$  atom and the pair of AO electrons of the carbonyl  $O$  atom. It is given as a linear combination of the energy contributions corresponding to a double bond,  $-1.13379 \text{ eV}$  (Eq. (14.247)), and a triple bond,  $-1.56513 \text{ eV}$  (Eq. (14.342)). The triple bond contribution includes the energy match of the carbonyl  $C2sp^3$  HO electron with the  $O$  of the  $C-O$ -bond MO in addition to the pair involved directly in the double bond with the carbonyl  $O$ .

$E_r(\text{atom} - \text{atom}, msp^3.AO)$  of the formic acid  $C=O$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $O$  atoms to the MO is  $-3.58557 \text{ eV}$ . This is also an energy minimum for the double bond between the pair of  $C2sp^3$  HO electrons of the  $C$  atom and the pair of AO electrons of the carbonyl  $O$  atom. It is given as a linear combination of the energy contributions corresponding to a triple bond,  $-1.56513 \text{ eV}$  (Eq. (14.342)), and a quadruple bond,  $-2.02043 \text{ eV}$  (Eqs. (15.18-15.21) with  $s=4$ ) where the bond order components are increased by an integer over that of alkyl carboxylic acids due to the presence of a  $H$  bound to the carbonyl carbon.

$E_r(\text{atom} - \text{atom}, msp^3.AO)$  of the carboxylic acid  $C-C(O)$  group is equivalent to that of alkanes and aldehydes,  $-1.85836 \text{ eV}$ , where both energy contributions are given by Eq. (14.513). It is based on the energy match between the  $C2sp^3$  HOs of the carboxylic acid. As in the case of aldehydes,  $C_{1o} = 2C_1$  in Eq. (15.52).

$E_r(\text{atom} - \text{atom}, msp^3.AO)$  of the carboxylic acid  $C-O$  group is equivalent to that of alkyl alcohols,  $-1.85836 \text{ eV}$ . It is based on the energy match between the  $O$  AO and the  $C2sp^3$  HO of a methylene group (the maximum hybridization for a single bond) where both energy contributions are given by Eq. (14.513).  $E_r(\text{atom} - \text{atom}, msp^3.AO)$  of the  $C-O$  group matches that of the  $C-C(O)$  group.

The symbols of the functional groups of alkyl carboxylic acids are given in Table 15.99. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acids are given in Tables 15.100, 15.101, and 15.102, respectively. The total energy of each alkyl carboxylic acid given in Table 15.103 was calculated as the sum over the integer multiple of each  $E_D(\text{group})$  of Table 15.102 corresponding to functional-group composition of the molecule. For each set of unpaired

electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_D(Group)$  (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of alkyl carboxylic acids determined using Eqs. (15.79-15.108) are given in Table 15.104.

Table 15.99. The symbols of functional groups of alkyl carboxylic acids.

| Functional Group            | Group Symbol     |
|-----------------------------|------------------|
| CH (formic acid) group      | $C-H$ (i)        |
| C-C(O)                      | $C-C(O)$         |
| C=O (formic acid)           | $C=O$ (i)        |
| C=O (alkyl carboxylic acid) | $C=O$ (ii)       |
| (O)C-O                      | $C-O$            |
| OH group                    | $OH$             |
| CH <sub>3</sub> group       | $C-H$ ( $CH_3$ ) |
| CH <sub>2</sub> group       | $C-H$ ( $CH_2$ ) |
| CH (alkyl) group            | $C-H$ (ii)       |
| CC bond (n-C)               | $C-C$ (a)        |
| CC bond (iso-C)             | $C-C$ (b)        |
| CC bond (tert-C)            | $C-C$ (c)        |
| CC (iso to iso-C)           | $C-C$ (d)        |
| CC (t to t-C)               | $C-C$ (e)        |
| CC (t to iso-C)             | $C-C$ (f)        |

Table 15.100. The geometrical bond parameters of alkyl carboxylic acids and experimental values [1].

| Parameter                | C-H (i)             | C-O (i)             | C=O (i)             | C=O (ii)            | OH                  | C-H (CH <sub>2</sub> ) | C-H (CH <sub>3</sub> ) | C-H (iii)         | C-C (a)         | C-C (b)         | C-C (c)         | C-C (d)         | C-C (e)         | C-C (f)         |
|--------------------------|---------------------|---------------------|---------------------|---------------------|---------------------|------------------------|------------------------|-------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| <i>a</i> (Å)             | 1.61341             | 2.04740             | 1.20799             | 1.29907             | 1.26430             | 1.67122                | 1.67122                | 1.67465           | 2.12499         | 2.12499         | 2.10725         | 2.12499         | 2.10725         | 2.10725         |
| <i>c'</i> (Å)            | 1.03711             | 1.43087             | 1.13613             | 1.13977             | 0.91803             | 1.04856                | 1.05553                | 1.05661           | 1.45744         | 1.45744         | 1.45164         | 1.45744         | 1.45164         | 1.45164         |
| Bond Length              | 1.09763             | 1.51437             | 1.20243             | 1.20628             | 0.971651            | 1.10974                | 1.11713                | 1.11827           | 1.54280         | 1.54280         | 1.53635         | 1.54280         | 1.53635         | 1.53635         |
| 2 <i>c'</i> (Å)          |                     |                     |                     |                     |                     |                        |                        |                   |                 |                 |                 |                 |                 |                 |
| Exp. Bond Length (Å)     | 1.097 (formic acid) | 1.520 (acetic acid) | 1.202 (formic acid) | 1.214 (acetic acid) | 0.972 (formic acid) | 1.107 (propane)        | 1.117 (propane)        | 1.122 (isobutane) | 1.532 (propane) | 1.532 (propane) | 1.531 (propane) | 1.532 (propane) | 1.531 (propane) | 1.532 (propane) |
| <i>h<sub>e</sub></i> (Å) | 1.23591             | 1.46439             | 0.61267             | 0.62331             | 1.12915             | 0.86925                | 0.63159                | 0.63095           | 1.54616         | 1.54616         | 1.52750         | 1.54616         | 1.52750         | 1.52750         |
| <i>c</i>                 | 0.64281             | 0.69887             | 0.88018             | 0.87737             | 0.75921             | 0.72615                | 0.63580                | 0.63095           | 0.68600         | 0.68600         | 0.68888         | 0.68600         | 0.68888         | 0.68888         |

Table 15.101. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acids. *E<sub>r</sub>* is *E<sub>r</sub>* (atom-atom, mpy, ÅO).

| Bond             | Atom | <i>E<sub>r</sub></i> (eV) Bond 1 | <i>E<sub>r</sub></i> (eV) Bond 2 | <i>E<sub>r</sub></i> (eV) Bond 3 | <i>E<sub>r</sub></i> (eV) Bond 4 | Final Total Energy (eV) | <i>r<sub>final</sub></i> (Å) | <i>r<sub>final</sub></i> (Å) | <i>E<sub>orbital</sub></i> (eV) Final | <i>E<sub>orbital</sub></i> (eV) Final | <i>θ'</i> (°) | <i>θ<sub>i</sub></i> (°) | <i>θ<sub>j</sub></i> (°) | <i>d<sub>i</sub></i> (Å) | <i>d<sub>j</sub></i> (Å) |
|------------------|------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|-------------------------|------------------------------|------------------------------|---------------------------------------|---------------------------------------|---------------|--------------------------|--------------------------|--------------------------|--------------------------|
| <i>RC</i> (O)O-H | O    | -0.92918                         | 0                                | 0                                | 0                                | -154.33766              | 1.00000                      | 0.86359                      | -15.75493                             | -15.75493                             | 115.09        | 64.91                    | 64.12                    | 0.55182                  | 0.56625                  |
| <i>HC</i> (O)O-H | O    | -0.92918                         | 0                                | 0                                | 0                                | -154.33766              | 1.00000                      | 0.86359                      | -15.75493                             | -15.75493                             | 101.32        | 78.68                    | 48.58                    | 1.14765                  | 0.16950                  |
| <i>HC</i> (O)O-H | C    | -0.92918                         | -1.79278                         | 0                                | 0                                | -154.33766              | 0.91771                      | 0.77536                      | -17.54772                             | -17.54772                             | 93.94         | 86.06                    | 43.24                    | 1.26386                  | 0.63329                  |
| <i>HC</i> (O)O-H | O    | -0.92918                         | 0                                | 0                                | 0                                | -154.33766              | 1.00000                      | 0.86359                      | -15.75493                             | -15.75493                             | 101.32        | 78.68                    | 48.58                    | 1.14765                  | 0.16950                  |
| <i>HC</i> (O)O-H | C    | -0.92918                         | -1.34946                         | -0.92918                         | 0                                | -154.33766              | 0.91771                      | 0.75447                      | -17.54772                             | -17.54772                             | 91.96         | 88.04                    | 41.90                    | 1.39138                  | 0.62578                  |
| <i>HC</i> (O)O-H | O    | -0.92918                         | 0                                | 0                                | 0                                | -154.33766              | 1.00000                      | 0.86359                      | -15.75493                             | -15.75493                             | 131.10        | 42.90                    | 65.45                    | 0.56355                  | 0.59978                  |
| <i>HC</i> (O)O-H | C    | -0.92918                         | -1.79278                         | 0                                | 0                                | -154.33766              | 0.91771                      | 0.77536                      | -17.54772                             | -17.54772                             | 133.24        | 44.76                    | 63.02                    | 0.38561                  | 0.55053                  |
| <i>HC</i> (O)O-H | O    | -0.92918                         | 0                                | 0                                | 0                                | -154.33766              | 1.00000                      | 0.86359                      | -15.75493                             | -15.75493                             | 137.27        | 42.73                    | 66.31                    | 0.21193                  | 0.61784                  |
| <i>HC</i> (O)O-H | C    | -0.92918                         | -1.34946                         | -0.92918                         | 0                                | -154.33766              | 0.91771                      | 0.75447                      | -17.54772                             | -17.54772                             | 133.47        | 46.53                    | 61.46                    | 0.20972                  | 0.51905                  |
| <i>HC</i> (O)O-H | O    | -0.92918                         | 0                                | 0                                | 0                                | -154.33766              | 1.00000                      | 0.86359                      | -15.75493                             | -15.75493                             | 110.11        | 36.09                    | 36.09                    | 1.30373                  | 0.26662                  |
| <i>HC</i> (O)O-H | C    | -0.92918                         | -1.34946                         | -0.92918                         | 0                                | -154.33766              | 0.91771                      | 0.75447                      | -17.54772                             | -17.54772                             | 123.75        | 123.75                   | 25.37                    | 1.85902                  | 0.41915                  |
| <i>HC</i> (O)O-H | O    | -0.92918                         | 0                                | 0                                | 0                                | -154.33766              | 1.00000                      | 0.86359                      | -15.75493                             | -15.75493                             | 107.73        | 107.73                   | 34.17                    | 1.03988                  | 0.32001                  |
| <i>HC</i> (O)O-H | C    | -0.92918                         | -1.34946                         | -0.92918                         | 0                                | -154.33766              | 0.91771                      | 0.75447                      | -17.54772                             | -17.54772                             | 65.99         | 114.01                   | 30.58                    | 1.76270                  | 0.33183                  |
| <i>HC</i> (O)O-H | O    | -0.92918                         | 0                                | 0                                | 0                                | -154.33766              | 1.00000                      | 0.86359                      | -15.75493                             | -15.75493                             | 77.49         | 102.31                   | 41.48                    | 1.25584                  | 0.18708                  |
| <i>HC</i> (O)O-H | C    | -0.92918                         | -1.34946                         | -0.92918                         | 0                                | -154.33766              | 0.91771                      | 0.75447                      | -17.54772                             | -17.54772                             | 111.55        | 111.55                   | 35.84                    | 1.35486                  | 0.29933                  |
| <i>HC</i> (O)O-H | O    | -0.92918                         | 0                                | 0                                | 0                                | -154.33766              | 1.00000                      | 0.86359                      | -15.75493                             | -15.75493                             | 61.10         | 118.90                   | 31.37                    | 1.42988                  | 0.37226                  |
| <i>HC</i> (O)O-H | C    | -0.92918                         | -1.34946                         | -0.92918                         | 0                                | -154.33766              | 0.91771                      | 0.75447                      | -17.54772                             | -17.54772                             | 63.82         | 116.18                   | 30.08                    | 1.85879                  | 0.38106                  |
| <i>HC</i> (O)O-H | O    | -0.92918                         | 0                                | 0                                | 0                                | -154.33766              | 1.00000                      | 0.86359                      | -15.75493                             | -15.75493                             | 56.41         | 123.59                   | 36.06                    | 1.90890                  | 0.45117                  |
| <i>HC</i> (O)O-H | C    | -0.92918                         | -1.34946                         | -0.92918                         | 0                                | -154.33766              | 0.91771                      | 0.75447                      | -17.54772                             | -17.54772                             | 131.70        | 131.70                   | 21.90                    | 1.97162                  | 0.51388                  |
| <i>HC</i> (O)O-H | O    | -0.92918                         | 0                                | 0                                | 0                                | -154.33766              | 1.00000                      | 0.86359                      | -15.75493                             | -15.75493                             | 131.79        | 131.79                   | 21.74                    | 1.95734                  | 0.50570                  |
| <i>HC</i> (O)O-H | C    | -0.92918                         | -1.34946                         | -0.92918                         | 0                                | -154.33766              | 0.91771                      | 0.75447                      | -17.54772                             | -17.54772                             | 131.70        | 131.70                   | 21.90                    | 1.97162                  | 0.51388                  |
| <i>HC</i> (O)O-H | O    | -0.92918                         | 0                                | 0                                | 0                                | -154.33766              | 1.00000                      | 0.86359                      | -15.75493                             | -15.75493                             | 129.96        | 129.96                   | 22.66                    | 1.94462                  | 0.49298                  |
| <i>HC</i> (O)O-H | C    | -0.92918                         | -1.34946                         | -0.92918                         | 0                                | -154.33766              | 0.91771                      | 0.75447                      | -17.54772                             | -17.54772                             | 50.04         | 139.96                   | 22.66                    | 1.94462                  | 0.49298                  |
| <i>HC</i> (O)O-H | O    | -0.92918                         | 0                                | 0                                | 0                                | -154.33766              | 1.00000                      | 0.86359                      | -15.75493                             | -15.75493                             | 52.78         | 137.22                   | 21.04                    | 1.93443                  | 0.47279                  |
| <i>HC</i> (O)O-H | C    | -0.92918                         | -1.34946                         | -0.92918                         | 0                                | -154.33766              | 0.91771                      | 0.75447                      | -17.54772                             | -17.54772                             | 50.04         | 139.96                   | 22.66                    | 1.94462                  | 0.49298                  |



Table 15.102. The energy parameters (eV) of functional groups of alkyl carboxylic acids

| Parameters   | C-H (i) | C-C (O) | C=O (i) | C=O (ii) | OH   | C-H <sub>2</sub> | C-H <sub>3</sub> | C-H (ii) | C-C (a) | C-C (b) | C-C (c) | C-C (d) | C-C (e) | C-C (f) |
|--------------|---------|---------|---------|----------|------|------------------|------------------|----------|---------|---------|---------|---------|---------|---------|
| $\eta_1$     | 1       | 1       | 2       | 2        | 1    | 3                | 2                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_2$     | 0       | 0       | 0       | 0        | 0    | 2                | 1                | 0        | 0       | 0       | 0       | 0       | 0       | 0       |
| $\eta_3$     | 0       | 0       | 0       | 0        | 0    | 0                | 0                | 0        | 0       | 0       | 0       | 0       | 0       | 0       |
| $\eta_4$     | 0       | 0       | 0       | 0        | 0    | 0                | 0                | 0        | 0       | 0       | 0       | 0       | 0       | 0       |
| $\eta_5$     | 0.75    | 0.5     | 0.5     | 0.5      | 0.75 | 0.75             | 0.75             | 0.75     | 0.5     | 0.5     | 0.5     | 0.5     | 0.5     | 0.5     |
| $\eta_6$     | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_7$     | 1       | 1       | 1       | 1        | 0.75 | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_8$     | 0.91771 | 0.91771 | 0.85395 | 0.85395  | 1    | 0.91771          | 0.91771          | 0.91771  | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 | 0.91771 |
| $\eta_9$     | 0       | 0       | 2       | 2        | 0    | 0                | 1                | 1        | 0       | 0       | 0       | 1       | 1       | 0       |
| $\eta_{10}$  | 1       | 2       | 4       | 4        | 1    | 1                | 1                | 1        | 2       | 2       | 2       | 2       | 2       | 2       |
| $\eta_{11}$  | 1       | 0       | 0       | 0        | 0    | 3                | 2                | 1        | 0       | 0       | 0       | 0       | 0       | 0       |
| $\eta_{12}$  | 0.75    | 0.5     | 0.5     | 0.5      | 0.75 | 0.75             | 0.75             | 0.75     | 0.5     | 0.5     | 0.5     | 0.5     | 0.5     | 0.5     |
| $\eta_{13}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{14}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{15}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{16}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{17}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{18}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{19}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{20}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{21}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{22}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{23}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{24}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{25}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{26}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{27}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{28}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{29}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{30}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{31}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{32}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{33}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{34}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{35}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{36}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{37}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{38}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{39}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{40}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{41}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{42}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{43}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{44}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{45}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{46}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{47}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{48}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{49}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{50}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{51}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{52}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{53}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{54}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{55}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{56}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{57}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{58}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{59}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{60}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{61}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{62}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{63}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{64}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{65}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{66}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{67}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{68}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{69}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{70}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{71}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{72}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{73}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{74}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{75}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{76}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{77}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{78}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{79}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{80}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{81}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{82}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{83}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{84}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{85}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{86}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{87}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{88}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{89}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{90}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{91}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{92}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{93}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{94}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{95}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{96}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{97}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{98}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{99}$  | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |
| $\eta_{100}$ | 1       | 1       | 1       | 1        | 1    | 1                | 1                | 1        | 1       | 1       | 1       | 1       | 1       | 1       |

Table 15.103. The total bond energies of alkyl carboxylic acids calculated using the functional group composition and the energies of Table 15.102 compared to the experimental values [3]. The magnetic energy  $E_{\text{mag}}$  that is subtracted from the weighted sum of the  $E_{\text{p}}(eV)$  values based on composition is given by (15.57).

| composition is given by (15.57).              |                            |         |         |         |          |    |                  |                  |          |         |         |         |         |         |         |                  |                                   |                                     |                |
|-----------------------------------------------|----------------------------|---------|---------|---------|----------|----|------------------|------------------|----------|---------|---------|---------|---------|---------|---------|------------------|-----------------------------------|-------------------------------------|----------------|
| Formula                                       | Name                       | C-H (i) | C-C (O) | C=O (i) | C=O (ii) | OH | C-H <sub>2</sub> | C-H <sub>3</sub> | C-H (ii) | C-C (a) | C-C (b) | C-C (c) | C-C (d) | C-C (e) | C-C (f) | E <sub>res</sub> | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
| CH <sub>3</sub> CO <sub>2</sub> H             | Formic acid                | 1       | 0       | 1       | 0        | 1  | 0                | 0                | 0        | 0       | 0       | 0       | 0       | 0       | 0       | 0                | 21.01945                          | 21.036                              | 0.00079        |
| C <sub>2</sub> H <sub>3</sub> O <sub>2</sub>  | Acetic acid                | 1       | 0       | 1       | 0        | 1  | 0                | 0                | 0        | 0       | 0       | 0       | 0       | 0       | 0       | 0                | 33.55916                          | 33.537                              | -0.00066       |
| C <sub>2</sub> H <sub>3</sub> O <sub>2</sub>  | Propionic acid             | 1       | 0       | 1       | 0        | 1  | 1                | 1                | 0        | 1       | 0       | 0       | 0       | 0       | 0       | 0                | 45.71686                          | 45.727                              | -0.00022       |
| C <sub>3</sub> H <sub>5</sub> O <sub>2</sub>  | Butyric acid               | 0       | 0       | 1       | 0        | 1  | 1                | 1                | 0        | 2       | 0       | 0       | 0       | 0       | 0       | 0                | 57.87456                          | 57.883                              | -0.00015       |
| C <sub>4</sub> H <sub>7</sub> O <sub>2</sub>  | Pentanoic acid             | 0       | 0       | 1       | 0        | 1  | 2                | 3                | 0        | 3       | 0       | 0       | 0       | 0       | 0       | 0                | 70.03236                          | 69.995                              | -0.00035       |
| C <sub>5</sub> H <sub>9</sub> O <sub>2</sub>  | 2,2-Dimethylpropanoic acid | 0       | 0       | 1       | 0        | 1  | 1                | 0                | 1        | 0       | 0       | 3       | 0       | 0       | 0       | 0                | 70.10482                          | 70.183                              | -0.00011       |
| C <sub>5</sub> H <sub>9</sub> O <sub>2</sub>  | 2,2-Dimethylpropanoic acid | 0       | 0       | 1       | 0        | 1  | 0                | 0                | 0        | 0       | 0       | 0       | 0       | 0       | 0       | -1               | 70.31679                          | 69.939                              | -0.00048       |
| C <sub>5</sub> H <sub>9</sub> O <sub>2</sub>  | Hexanoic acid              | 0       | 0       | 1       | 0        | 1  | 2                | 4                | 0        | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 82.18996                          | 82.149                              | -0.00039       |
| C <sub>5</sub> H <sub>9</sub> O <sub>2</sub>  | Heptanoic acid             | 0       | 0       | 1       | 0        | 1  | 3                | 5                | 0        | 5       | 0       | 0       | 0       | 0       | 0       | 0                | 94.34766                          | 94.147                              | -0.00040       |
| C <sub>6</sub> H <sub>11</sub> O <sub>2</sub> | Octanoic acid              | 0       | 0       | 1       | 0        | 1  | 4                | 6                | 0        | 6       | 0       | 0       | 0       | 0       | 0       | 0                | 106.58336                         | 106.481                             | -0.00022       |
| C <sub>6</sub> H <sub>11</sub> O <sub>2</sub> | Nonanoic acid              | 0       | 0       | 1       | 0        | 1  | 5                | 7                | 0        | 7       | 0       | 0       | 0       | 0       | 0       | 0                | 118.82006                         | 118.696                             | -0.00056       |
| C <sub>6</sub> H <sub>11</sub> O <sub>2</sub> | Decanoic acid              | 0       | 0       | 1       | 0        | 1  | 6                | 8                | 0        | 8       | 0       | 0       | 0       | 0       | 0       | 0                | 130.99076                         | 130.795                             | -0.00020       |
| C <sub>6</sub> H <sub>11</sub> O <sub>2</sub> | Dodecanoic acid            | 0       | 0       | 1       | 0        | 1  | 7                | 9                | 0        | 9       | 0       | 0       | 0       | 0       | 0       | 0                | 152.13616                         | 152.176                             | 0.00026        |
| C <sub>6</sub> H <sub>11</sub> O <sub>2</sub> | Tetradecanoic acid         | 0       | 0       | 1       | 0        | 1  | 8                | 10               | 0        | 10      | 0       | 0       | 0       | 0       | 0       | 0                | 173.45156                         | 173.605                             | 0.00085        |
| C <sub>6</sub> H <sub>11</sub> O <sub>2</sub> | Hexadecanoic acid          | 0       | 0       | 1       | 0        | 1  | 9                | 11               | 0        | 11      | 0       | 0       | 0       | 0       | 0       | 0                | 191.62926                         | 191.666                             | -0.00002       |
| C <sub>6</sub> H <sub>11</sub> O <sub>2</sub> | Octadecanoic acid          | 0       | 0       | 1       | 0        | 1  | 10               | 12               | 0        | 12      | 0       | 0       | 0       | 0       | 0       | 0                | 203.76696                         | 203.948                             | 0.00089        |
| C <sub>6</sub> H <sub>11</sub> O <sub>2</sub> | Stearic acid               | 0       | 0       | 1       | 0        | 1  | 11               | 13               | 0        | 13      | 0       | 0       | 0       | 0       | 0       | 0                | 228.08336                         | 228.298                             | 0.00094        |
| C <sub>6</sub> H <sub>11</sub> O <sub>2</sub> | Arachidic acid             | 0       | 0       | 1       | 0        | 1  | 16               | 0                | 0        | 16      | 0       | 0       | 0       | 0       | 0       | 0                | 252.39776                         | 252.514                             | 0.00045        |

Table 15.104. The bond angle parameters of alkyl carboxylic acids and experimental values [1]. In the calculation of  $\theta_i$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{resp. } \text{AO})$ .

| Atom of Angle | $2\sigma_1$<br>( $\sigma_1$ ) | $2\sigma_2$<br>( $\sigma_2$ ) | $2\sigma_3$<br>( $\sigma_3$ ) | $F_{\text{Hybridization}}$<br>Atom 1<br>(Table 15.1 A) | $F_{\text{Hybridization}}$<br>Atom 2<br>(Table 15.1 A) | $F_{\text{Hybridization}}$<br>Atom 3<br>(Table 15.1 A) | $c_1$<br>Atom 1 | $c_2$<br>Atom 2           | $c_3$<br>Atom 3           | $\zeta_1$ | $\zeta_2$ | $\zeta_3$ | $E_T$<br>(eV) | $\theta_i$<br>( $^\circ$ ) | $\theta_j$<br>( $^\circ$ ) | $\theta_k$<br>( $^\circ$ ) | Cal. $\theta$<br>( $^\circ$ ) | Exp. $\theta$<br>( $^\circ$ ) |
|---------------|-------------------------------|-------------------------------|-------------------------------|--------------------------------------------------------|--------------------------------------------------------|--------------------------------------------------------|-----------------|---------------------------|---------------------------|-----------|-----------|-----------|---------------|----------------------------|----------------------------|----------------------------|-------------------------------|-------------------------------|
| $ZHC(O)_2$    | 2.06398                       | 2.27227                       | 3.9816                        | -15.55033<br>$C_s$                                     | -15.55033<br>$C_s$                                     | -15.55033<br>$C_s$                                     | 0.87495         | 0.83595<br>(Eq. (15.114)) | 0.83595<br>(Eq. (15.114)) | 0.75      | 1         | 0.75      | 0             |                            |                            |                            | 126.88                        | 124.1<br>(formic acid)        |
| $ZHC(O)_2$    | 2.06398                       | 2.63431                       | 3.9816                        | -15.55033<br>$C_s$                                     | -15.55033<br>$C_s$                                     | -15.55033<br>$C_s$                                     | 0.87495         | 0.83595<br>(Eq. (15.114)) | 0.83595<br>(Eq. (15.114)) | 0.75      | 1         | 0.75      | 0             |                            |                            |                            | 110.76                        |                               |
| $ZOC(O)_2$    | 2.27227                       | 2.63431                       | 4.3243                        | -16.61853<br>$O_s$                                     | -15.75493<br>$O_s$                                     | -15.75493<br>$O_s$                                     | 0.81871         | 0.86359                   | 0.86359                   | 1         | 1         | 1         | -1.4915       |                            |                            |                            | 123.44                        | 124.9<br>(formic acid)        |
| $ZC(O)_2H$    | 2.63431                       | 1.85616                       | 3.6405                        | -14.82575<br>$C_s$                                     | -14.82575<br>$C_s$                                     | -14.82575<br>$C_s$                                     | 1               | 0.91771                   | 0.91771                   | 0.75      | 1         | 0.75      | 0             |                            |                            |                            | 107.71                        | 106.3<br>(formic acid)        |
| $ZC(O)_2H$    | 2.8675                        | 2.27954                       | 4.3826                        | -16.0411<br>$C_s$                                      | -13.61896<br>$O_s$                                     | -13.61896<br>$O_s$                                     | 0.81549         | 0.83595<br>(Eq. (15.114)) | 0.83595<br>(Eq. (15.114)) | 1         | 1         | 1         | -1.6376       |                            |                            |                            | 125.70                        | 126.6<br>(acetic acid)        |
| $ZC(O)_2H$    | 2.8675                        | 2.63431                       | 4.914                         | -15.75493<br>$O_s$                                     | -13.61896<br>$O_s$                                     | -13.61896<br>$O_s$                                     | 0.86359         | 0.83595<br>(Eq. (15.114)) | 0.83595<br>(Eq. (15.114)) | 1         | 1         | 1         | -1.4915       |                            |                            |                            | 109.65                        | 110.8<br>(acetic acid)        |
| $ZOC(O)_2$    | 2.27954                       | 2.63431                       | 4.3818                        | -16.7521<br>$O_s$                                      | -15.75493<br>$O_s$                                     | -15.75493<br>$O_s$                                     | 0.84115         | 0.86359                   | 0.86359                   | 1         | 1         | 1         | -1.4915       |                            |                            |                            | 126.03                        |                               |
| $ZHC(O)_2$    | 2.1106                        | 2.1106                        | 3.4252                        | -15.75493<br>$C_s$                                     | -15.75493<br>$C_s$                                     | -15.75493<br>$C_s$                                     | 0.86359         | 1                         | 1                         | 1         | 1         | 0.75      | 0             |                            |                            |                            | 108.44                        | 107<br>(propionic)            |
| $ZC(O)_2C$    |                               |                               |                               |                                                        |                                                        |                                                        |                 |                           |                           |           |           |           |               | 69.51                      |                            |                            |                               | 112<br>(propionic)            |
| $ZC(O)_2H$    |                               |                               |                               |                                                        |                                                        |                                                        |                 |                           |                           |           |           |           |               |                            |                            |                            |                               | 113.8<br>(butanoic)           |
| $ZC(O)_2C$    | 2.09711                       | 2.09711                       | 3.4252                        | -15.75493<br>$C_s$                                     | -15.75493<br>$C_s$                                     | -15.75493<br>$C_s$                                     | 0.86359         | 1                         | 1                         | 1         | 1         | 0.75      | 0             |                            |                            |                            | 109.50                        | 110.4<br>(butanoic)           |
| $ZC(O)_2H$    |                               |                               |                               |                                                        |                                                        |                                                        |                 |                           |                           |           |           |           |               | 70.56                      |                            |                            |                               | 109.44<br>(butanoic)          |
| $ZC(O)_2C$    | 2.91547                       | 2.91547                       | 4.7958                        | -16.0412<br>$C_s$                                      | -16.0412<br>$C_s$                                      | -16.0412<br>$C_s$                                      | 0.81549         | 0.81549                   | 0.81549                   | 1         | 1         | 1         | -1.8356       |                            |                            |                            | 110.67                        | 110.8<br>(butanoic)           |
| $ZC(O)_2H$    | 2.91547                       | 2.11325                       | 4.1633                        | -15.50033<br>$C_s$                                     | -14.82575<br>$C_s$                                     | -14.82575<br>$C_s$                                     | 0.87495         | 0.91771                   | 0.91771                   | 0.75      | 1         | 0.75      | 0             |                            |                            |                            | 110.76                        |                               |
| $ZC(O)_2H$    | 2.91547                       | 2.69711                       | 4.1633                        | -15.50033<br>$C_s$                                     | -14.82575<br>$C_s$                                     | -14.82575<br>$C_s$                                     | 0.87495         | 0.91771                   | 0.91771                   | 0.75      | 1         | 0.75      | 0             |                            |                            |                            | 111.27                        | 111.4<br>(butanoic)           |
| $ZC(O)_2C$    | 2.90327                       | 2.90327                       | 4.7958                        | -15.50033<br>$C_s$                                     | -14.82575<br>$C_s$                                     | -14.82575<br>$C_s$                                     | 0.87495         | 0.91771                   | 0.91771                   | 0.75      | 1         | 0.75      | -1.8356       |                            |                            |                            | 111.27                        | 111.4<br>(butanoic)           |
| $ZC(O)_2C$    |                               |                               |                               |                                                        |                                                        |                                                        |                 |                           |                           |           |           |           |               | 72.50                      |                            |                            | 107.50                        |                               |

CARBOXYLIC ACID ESTERS ( $C_nH_{2n}O_2$ ,  $n = 1, 2, 3, 4, 5 \dots \infty$ )

The alkyl carboxylic acid esters,  $C_nH_{2n}O_2$ , comprise a  $C=O$  functional group, and the single bond of carbon to the carbonyl carbon atom,  $C-C(O)$ , is also a functional group. Formic acid ester has a  $HC=O$  moiety that comprises a more stable  $C=O$  functional group and a  $CH$  functional group. All carboxylic acid esters further comprise a  $COR$  moiety that comprises a  $C-O$  functional group and three types of  $O-R$  functional groups, one for  $R$  comprising methyl, one for  $R$  comprising an alkyl ester group of a formate, and one for  $R$  comprising an alkyl ester group of an alkyl carboxylate. The alkyl portion of the alkyl carboxylic acid ester may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acid esters are equivalent to those in branched-chain alkanes.

The  $CH$  functional group is equivalent to that of formic acid. The alkyl carboxylic acid ester  $C=O$  and  $C-C(O)$  groups are equivalent to those given in the Carboxylic Acids section. The formic acid ester  $C=O$  group is equivalent to that given in the Carboxylic Acids section except that  $\bar{E}_{Kvib}$  is that corresponding to a formic acid ester. The  $C-O$  group is equivalent to that given in the Carboxylic Acids section except that the parameters corresponding to oscillation of the bond in the transition state,  $\bar{E}_D$  (eV) and  $\bar{E}_{Kvib}$ , are those of a carboxylic acid ester. As in the case with the alkyl ethers, each  $O-C$  group is solved by hybridizing the  $2s$  and  $2p$  AOs of the  $C$  atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the  $O$  AO to form a MO permits each participating orbital to decrease in radius and energy. To meet the equipotential condition of the union of the  $O-C$   $H_2$ -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor  $c_2$  of Eq. (15.51) for the  $O-C$ -bond MO given by Eq. (15.114) is  $c_2(C2sp^3HO \text{ to } O) = 0.85395$ .

$E_T(\text{atom} - \text{atom}, msp^3.AO)$  (Eq. (15.52)) of (1) the  $C = O$  group of alkyl carboxylic acid esters, (2) the  $C = O$  group of formic acid esters, (3) the alkyl carboxylic acid ester  $C - C(O)$  group, and (4) the carboxylic acid ester  $C - O$  group are equivalent to those of the corresponding carboxylic acids. The values given in the Carboxylic Acids section are  
 5  $-2.69893 \text{ eV}$ ,  $-3.58557 \text{ eV}$ ,  $-1.85836 \text{ eV}$ , and  $-1.85836 \text{ eV}$ , respectively.  
 $E_T(\text{atom} - \text{atom}, msp^3.AO)$  of the  $C - O$  group matches that of the  $C - C(O)$  group. Also, as in the case of aldehydes,  $C_{1o} = 2C_1$  in Eq. (15.52) for the  $C - C(O)$  group.

$E_T(\text{atom} - \text{atom}, msp^3.AO)$  of the  $O - C$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $O$  atoms to the MO is  $-1.13379 \text{ eV}$  for the  $O - CH_3$  group of  
 10 formate and alkyl carboxylates,  $-1.44915 \text{ eV}$  for the  $O - R$  group of alkyl carboxylates, and  $-1.85836 \text{ eV}$  for the  $O - R$  group of alkyl formates, where  $R$  is an alkyl group. Each is based on the energy match between the  $O$  AO, initially at the Coulomb potential of a proton and an electron (Eqs. (1.236) and (10.162), respectively), the  $C2sp^3$  HO of the methyl or alkyl ester group, and the carbonyl carbon. The increasing energy contributions to the single bond  
 15 correspond to the increasing hybridization of linear combinations of increasing bond order. The energy contributions corresponding to one half of a double bond and those of the methyl-methyl and methylene-methylene bonds are  $-1.13379 \text{ eV}$  (Eq. (14.247)), two times  $-0.72457 \text{ eV}$  (Eq. (14.151)), and two times  $-0.92918 \text{ eV}$  (Eq. (14.513)), respectively.

The symbols of the functional groups of alkyl carboxylic acid esters are given in Table  
 20 15.105. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acid esters are given in Tables 15.106, 15.107, and 15.108, respectively. The total energy of each alkyl carboxylic acid ester given in Table 15.109 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.108 corresponding to functional-group composition of the  
 25 molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_D(\text{Group})$  ( $\text{eV}$ ) values based on composition is given by Eq. (15.58). The bond angle parameters of alkyl carboxylic acid esters determined using Eqs. (15.79-15.108) are given in Table 15.110.

Table 15.105. The symbols of functional groups of alkyl carboxylic acid esters.

| Functional Group                  | Group Symbol     |
|-----------------------------------|------------------|
| CH (formic acid ester) group      | $C-H$ (i)        |
| C-C(O)                            | $C-C(O)$         |
| C=O (formic acid ester)           | $C=O$ (i)        |
| C=O (alkyl carboxylic acid ester) | $C=O$ (ii)       |
| (O)C-O                            | $C-O$            |
| O-CH <sub>3</sub>                 | $O-C$ (i)        |
| O-R (formic acid ester)           | $O-C$ (ii)       |
| O-R (alkyl acid ester)            | $O-C$ (iii)      |
| OH group                          | $OH$             |
| CH <sub>3</sub> group             | $C-H$ ( $CH_3$ ) |
| CH <sub>2</sub> group             | $C-H$ ( $CH_2$ ) |
| CH (alkyl) group                  | $C-H$ (ii)       |
| CC bond (n-C)                     | $C-C$ (a)        |
| CC bond (iso-C)                   | $C-C$ (b)        |
| CC bond (tert-C)                  | $C-C$ (c)        |
| CC (iso to iso-C)                 | $C-C$ (d)        |
| CC (t to t-C)                     | $C-C$ (e)        |
| CC (t to iso-C)                   | $C-C$ (f)        |

Table 15.106. The geometrical bond parameters of alkyl carboxylic acid esters and experimental values [1].

| Parameter                | C-H (i)<br>Group          | C-C(O)<br>Group        | C=O (i)<br>Group          | C=O (ii)<br>Group      | C-O<br>Group                   | O-C (i)<br>Group               | O-C (ii)<br>Group              | O-C (iii)<br>Group             | C-H (CH <sub>3</sub> )<br>Group                                                                                                | C-H (CH <sub>2</sub> )<br>Group                 | C-C (a)<br>Group                        | C-C (b)<br>Group                        | C-C (c)<br>Group                        | C-C (d)<br>Group                        | C-C (e)<br>Group                        | C-C (f)<br>Group                        |
|--------------------------|---------------------------|------------------------|---------------------------|------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|
| $a$ (Å)                  | 1.6134                    | 2.04740                | 1.290799                  | 1.29907                | 1.73490                        | 1.82683                        | 1.78255                        | 1.80717                        | 1.64920                                                                                                                        | 1.67122                                         | 2.12499                                 | 2.12499                                 | 2.10725                                 | 2.12499                                 | 2.10725                                 | 2.10725                                 |
| $c'$ (Å)                 | 1.03711                   | 1.43087                | 1.13613                   | 1.13977                | 1.31716                        | 1.35160                        | 1.35112                        | 1.34431                        | 1.04856                                                                                                                        | 1.05553                                         | 1.45744                                 | 1.45744                                 | 1.45164                                 | 1.45744                                 | 1.45164                                 | 1.45164                                 |
| Bond Length<br>$2c'$ (Å) | 1.09763                   | 1.51437                | 1.20243                   | 1.20628                | 1.39402                        | 1.43047                        | 1.41303                        | 1.42276                        | 1.10974                                                                                                                        | 1.11713                                         | 1.54280                                 | 1.54280                                 | 1.53635                                 | 1.54280                                 | 1.53635                                 | 1.53635                                 |
| Exp. Bond Length<br>(Å)  | 1.101<br>(methyl formate) | 1.520<br>(acetic acid) | 1.206<br>(methyl formate) | 1.214<br>(acetic acid) | 1.393<br>(avg. methyl formate) | 1.393<br>(avg. methyl formate) | 1.393<br>(avg. methyl formate) | 1.393<br>(avg. methyl formate) | 1.08<br>(methyl formate)<br>1.107<br>(C-H propane)<br>1.107<br>(C-H propane)<br>1.117<br>(C-H butane)<br>1.117<br>(C-H butane) | 1.107<br>(C-H propane)<br>1.117<br>(C-H butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $b, c$ (Å)               | 1.23591                   | 1.46439                | 0.61267                   | 0.62331                | 1.12915                        | 1.22901                        | 1.18107                        | 1.20776                        | 1.27295                                                                                                                        | 1.29569                                         | 1.54616                                 | 1.54616                                 | 1.52750                                 | 1.54616                                 | 1.52750                                 | 1.52750                                 |
| $e$                      | 0.64281                   | 0.69887                | 0.88078                   | 0.87737                | 0.75921                        | 0.73986                        | 0.74900                        | 0.74388                        | 0.63580                                                                                                                        | 0.63159                                         | 0.68600                                 | 0.68600                                 | 0.68888                                 | 0.68600                                 | 0.68888                                 | 0.68888                                 |

Table 15.107. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acid esters.  $R, R', R''$  are H or alkyl groups.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{msp}, \text{AO})$ .

| Bond                                    | Atom           | $E_T$<br>(eV)<br>Bond 1 | $E_T$<br>(eV)<br>Bond 2 | $E_T$<br>(eV)<br>Bond 3 | $E_T$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>C2sp <sup>2</sup><br>(eV) | $r_{\text{bond}}$<br>( $a_0$ ) | $r_{\text{bond}}$<br>( $a_0$ ) | $E_{\text{orbital}}$<br>(eV)<br>Final | $E(\text{C2sp}^2)$<br>(eV)<br>Final | $\theta_1$<br>(°) | $\theta_2$<br>(°) | $d_1$<br>( $a_0$ ) | $d_2$<br>( $a_0$ ) |
|-----------------------------------------|----------------|-------------------------|-------------------------|-------------------------|-------------------------|----------------------------------------------------|--------------------------------|--------------------------------|---------------------------------------|-------------------------------------|-------------------|-------------------|--------------------|--------------------|
| $RC_1(O)O-C_1H_3$<br>(O-C (i))          | O              | -0.92918                | -0.56690                | 0                       | 0                       |                                                    | 1.00000                        | 0.83360                        | -16.32183                             |                                     | 89.37             | 42.70             | 1.34246            | 0.00914            |
| $RC_1(O)O-C_1H_3$<br>(O-C (i))          | C <sub>1</sub> | -0.56690                | 0                       | 0                       | 0                       | -152.18259                                         | 0.91771                        | 0.88392                        | -15.39265                             | -15.20178                           | 84.99             | 45.76             | 1.27445            | 0.07716            |
| $HC_1(O)O-C_1H_2C_1H_2R$<br>(O-C (iii)) | O              | -0.92918                | -0.92918                | 0                       | 0                       |                                                    | 1.00000                        | 0.81549                        | -16.68412                             |                                     | 86.91             | 43.59             | 1.29113            | 0.04399            |
| $HC_1(O)O-C_1H_2C_1H_2R$<br>(O-C (iii)) | C <sub>1</sub> | -0.92918                | -0.92918                | 0                       | 0                       | -153.74005                                         | 0.91771                        | 0.81549                        | -16.68411                             | -16.49325                           | 86.91             | 43.59             | 1.29113            | 0.04399            |
| $RC_1(O)O-C_1H_2C_1H_2R$<br>(O-C (iii)) | O              | -0.92918                | -0.72457                | 0                       | 0                       |                                                    | 1.00000                        | 0.82562                        | -16.47951                             |                                     | 88.28             | 43.10             | 1.31951            | 0.02480            |
| $RC_1(O)O-C_1H_2C_1H_2R$<br>(O-C (iii)) | C <sub>1</sub> | -0.72457                | -0.92918                | 0                       | 0                       | -153.26945                                         | 0.91771                        | 0.82562                        | -16.47951                             | -16.28864                           | 88.28             | 43.10             | 1.31951            | 0.02480            |
| $HC_1(O)O-C_1H_3$<br>(C=O (i))          | O              | -0.92918                | -0.56690                | 0                       | 0                       |                                                    | 1.00000                        | 0.83360                        | -16.32183                             |                                     | 89.37             | 46.82             | 1.18716            | 0.13300            |
| $HC_1(O)O-C_1H_3$<br>(C=O (i))          | C <sub>1</sub> | -0.56690                | -1.79278                | 0                       | 0                       | -154.33765                                         | 0.91771                        | 0.77556                        | -17.54772                             | -17.35685                           | 86.06             | 43.24             | 1.26386            | 0.05329            |
| $HC_1(O)O-C_1H_3$<br>(O-C (i))          | O              | -0.92918                | -0.92918                | 0                       | 0                       |                                                    | 1.00000                        | 0.81549                        | -16.68412                             |                                     | 82.52             | 45.73             | 1.21100            | 0.10616            |
| $HC_1(O)O-C_1H_3$<br>(O-C (i))          | C <sub>1</sub> | -1.79278                | -0.92918                | 0                       | 0                       | -154.33765                                         | 0.91771                        | 0.77556                        | -17.54772                             | -17.35685                           | 86.06             | 43.24             | 1.26386            | 0.05329            |
| $R'H_1C_1C_1(O)-OC_1H_3$<br>(C=O (ii))  | O              | -0.92918                | -0.56690                | 0                       | 0                       |                                                    | 1.00000                        | 0.83360                        | -16.32183                             |                                     | 89.37             | 46.82             | 1.18716            | 0.13300            |
| $R'H_1C_1C_1(O)-OC_1H_3$<br>(C=O (ii))  | C <sub>1</sub> | -0.92918                | -1.34946                | -0.92918                | 0                       | -154.82352                                         | 0.91771                        | 0.75447                        | -18.03358                             | -17.84271                           | 88.04             | 41.90             | 1.29138            | 0.02578            |
| $R'H_1C_1C_1(O)-OC_1H_3$<br>(O-C (ii))  | O              | -0.92918                | -0.72457                | 0                       | 0                       |                                                    | 1.00000                        | 0.82562                        | -16.47951                             |                                     | 81.68             | 46.34             | 1.19766            | 0.11949            |
| $R'H_1C_1C_1(O)-OC_1H_3$<br>(O-C (ii))  | C <sub>1</sub> | -0.72457                | -0.92918                | -0.92918                | 0                       | -154.82352                                         | 0.91771                        | 0.75447                        | -18.03358                             | -17.84271                           | 88.04             | 41.90             | 1.29138            | 0.02578            |
| $HC_1(O)R=O$<br>(C=O (i))               | O              | -1.79278                | 0                       | 0                       | 0                       |                                                    | 1.00000                        | 0.81871                        | -16.61853                             |                                     | 137.10            | 63.45             | 0.53635            | 0.59978            |
| $HC_1(O)R=O$<br>(C=O (i))               | C <sub>1</sub> | -1.79278                | -0.92918                | 0                       | 0                       | -154.33766                                         | 0.91771                        | 0.77556                        | -17.54772                             | -17.35685                           | 44.76             | 63.02             | 0.38561            | 0.55053            |
| $R'C_1H_2C_1(O)R=O$<br>(C=O (ii))       | O              | -1.34946                | -0.92918                | 0                       | 0                       |                                                    | 1.00000                        | 0.84115                        | -16.17521                             |                                     | 137.27            | 66.31             | 0.32193            | 0.61784            |
| $R'C_1H_2C_1(O)R=O$<br>(C=O (ii))       | C <sub>1</sub> | -1.34946                | -0.92918                | -0.92918                | 0                       | -154.82352                                         | 0.91771                        | 0.75447                        | -18.03358                             | -17.84272                           | 133.47            | 61.46             | 0.62072            | 0.51905            |
| $H-C(O)OR$<br>(C H (i))                 | C              | -1.79278                | -0.92918                | 0                       | 0                       | -154.33766                                         | 0.91771                        | 0.77556                        | -17.54772                             | -17.35685                           | 69.89             | 110.11            | 1.30373            | 0.26662            |
| $R'H_1C_1-C_1(O)OR$<br>(C H (i))        | C <sub>1</sub> | -0.92918                | -1.34946                | -0.92918                | 0                       | -154.82352                                         | 0.91771                        | 0.75447                        | -18.03358                             | -17.84272                           | 56.25             | 123.75            | 1.85002            | 0.41915            |
| $H_1C_1-C_1(O)OR$<br>(C H (i))          | C <sub>1</sub> | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                         | 0.91771                        | 0.86359                        | -15.75495                             | -15.56407                           | 72.27             | 107.75            | 1.63888            | 0.26501            |
| $R'H_1C_1H_2C_1-C_1(O)OR$<br>(C H (i))  | C <sub>1</sub> | -0.92918                | -0.92918                | 0                       | 0                       | -153.47405                                         | 0.91771                        | 0.81549                        | -16.68411                             | -16.49325                           | 68.91             | 114.01            | 1.70270            | 0.33183            |
| $C-H (CH_3)$<br>(C H (i))               | C              | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                         | 0.91771                        | 0.86359                        | -15.75495                             | -15.56407                           | 77.49             | 102.51            | 1.23564            | 0.18708            |
| $C-H (CH_2)$<br>(C H (i))               | C              | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                         | 0.91771                        | 0.81549                        | -16.68412                             | -16.49325                           | 68.47             | 111.53            | 1.35486            | 0.29953            |

| Bond                   | Atom           | $E_r$<br>(eV)<br>Bond 1 | $E_r$<br>(eV)<br>Bond 2 | $E_r$<br>(eV)<br>Bond 3 | $E_r$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>$C_{2sp^3}$<br>(eV) | $r_{final}$<br>( $a_0$ ) | $r_{final}$<br>( $a_0$ ) | $E_{calculated}$<br>(eV)<br>Final | $E(C_{2sp^3})$<br>(eV)<br>Final | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | $d_1$<br>( $a_0$ ) | $d_2$<br>( $a_0$ ) |
|------------------------|----------------|-------------------------|-------------------------|-------------------------|-------------------------|----------------------------------------------|--------------------------|--------------------------|-----------------------------------|---------------------------------|----------------------------|----------------------------|--------------------|--------------------|
| $C-H$ (i)              | C              | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                   | 0.91771                  | 0.77247                  | -17.61330                         | -17.42244                       | 118.90                     | 31.37                      | 1.42988            | 0.37526            |
| $H_1C_1C_2H_2$ (ii)    | C <sub>1</sub> | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                   | 0.91771                  | 0.86359                  | -15.75493                         | -15.56407                       | 116.18                     | 30.08                      | 1.83879            | 0.38106            |
| $H_1C_1C_2H_2$ (iii)   | C <sub>2</sub> | -0.92918                | -0.92918                | 0                       | 0                       | -153.47906                                   | 0.91771                  | 0.81549                  | -16.68412                         | -16.49325                       | 125.59                     | 26.06                      | 1.50890            | 0.45117            |
| $R-H_1C_1C_2H_2$ (iv)  | C <sub>1</sub> | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                   | 0.91771                  | 0.77247                  | -17.61330                         | -17.42244                       | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| $R-H_1C_1C_2H_2$ (v)   | C <sub>2</sub> | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -154.71860                                   | 0.91771                  | 0.73889                  | -17.92866                         | -17.73779                       | 131.79                     | 21.74                      | 1.95734            | 0.50570            |
| $rac-C_1C_2H_2$ (vi)   | C <sub>1</sub> | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                   | 0.91771                  | 0.77247                  | -17.61330                         | -17.42244                       | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| $rac-C_1C_2H_2$ (vii)  | C <sub>2</sub> | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -154.51399                                   | 0.91771                  | 0.76765                  | -17.92866                         | -17.73779                       | 129.96                     | 22.66                      | 1.94462            | 0.49298            |
| $rac-C_1C_2H_2$ (viii) | C <sub>1</sub> | -0.72457                | -0.72457                | -0.92918                | 0                       | -154.19863                                   | 0.91771                  | 0.78155                  | -17.40869                         | -17.21785                       | 127.22                     | 24.04                      | 1.92443            | 0.47279            |
| $rac-C_1C_2H_2$ (ix)   | C <sub>2</sub> | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.13599                                   | 0.91771                  | 0.76765                  | -17.92866                         | -17.73779                       | 129.96                     | 22.66                      | 1.94462            | 0.49298            |



Table 15.108. The energy parameters (eV) of functional groups of alkyl carboxylic acid esters.

| Parameters                             | C-H (i)   | C-C(O)    | C=O (i)    | C=O (ii)   | O-C (i)   | O-C (ii)  | O-C (iii) | CH <sub>3</sub> | CH <sub>2</sub> | C-H (ii)  | C-C (a)   | C-C (b)   | C-C (c)   | C-C (d)   | C-C (e)   | C-C (f)   |
|----------------------------------------|-----------|-----------|------------|------------|-----------|-----------|-----------|-----------------|-----------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| $n_1$                                  | 1         | 1         | 2          | 2          | 1         | 1         | 1         | 3               | 2               | 1         | 1         | 1         | 1         | 1         | 1         | 1         |
| $n_2$                                  | 0         | 0         | 0          | 0          | 0         | 0         | 0         | 2               | 1               | 0         | 0         | 0         | 0         | 0         | 0         | 0         |
| $n_3$                                  | 0         | 0         | 0          | 0          | 0         | 0         | 0         | 0               | 0               | 0         | 0         | 0         | 0         | 0         | 0         | 0         |
| $C_1$                                  | 0.75      | 0.5       | 0.5        | 0.5        | 0.5       | 0.5       | 0.5       | 0.75            | 0.75            | 0.75      | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       |
| $C_2$                                  | 1         | 1         | 1          | 1          | 1         | 1         | 1         | 1               | 1               | 1         | 1         | 1         | 1         | 1         | 1         | 1         |
| $C_3$                                  | 1         | 1         | 1          | 1          | 1         | 1         | 1         | 1               | 1               | 1         | 1         | 1         | 1         | 1         | 1         | 1         |
| $C_4$                                  | 0.91771   | 0.91771   | 0.85395    | 0.85395    | 0.85395   | 0.85395   | 0.85395   | 0.91771         | 0.91771         | 0.91771   | 0.91771   | 0.91771   | 0.91771   | 0.91771   | 0.91771   | 0.91771   |
| $C_5$                                  | 0         | 0         | 2          | 2          | 0         | 0         | 0         | 0               | 1               | 1         | 0         | 0         | 0         | 1         | 1         | 0         |
| $C_6$                                  | 1         | 2         | 4          | 4          | 2         | 2         | 2         | 1               | 1               | 1         | 2         | 2         | 2         | 2         | 2         | 2         |
| $C_7$                                  | 1         | 0         | 0          | 0          | 0         | 0         | 0         | 3               | 2               | 1         | 0         | 0         | 0         | 0         | 0         | 0         |
| $C_{10}$                               | 0.75      | 1         | 0.5        | 0.5        | 0.5       | 0.5       | 0.5       | 0.75            | 0.75            | 0.75      | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       |
| $C_{20}$                               | 1         | 1         | 1          | 1          | 1         | 1         | 1         | 1               | 1               | 1         | 1         | 1         | 1         | 1         | 1         | 1         |
| $V_e$ (eV)                             | -36.74167 | -30.19634 | -112.61934 | -111.25473 | -35.08488 | -32.67173 | -33.78830 | -107.32728      | -70.41425       | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_p$ (eV)                             | 13.11890  | 9.50874   | 23.95107   | 23.97467   | 10.32968  | 10.06642  | 10.19070  | 38.92728        | 25.78002        | 12.87680  | 9.33352   | 9.33352   | 9.37273   | 9.33352   | 9.37273   | 9.37273   |
| $T$ (eV)                               | 11.38634  | 7.37432   | 43.62389   | 42.82081   | 10.11150  | 8.94219   | 9.47754   | 32.55914        | 21.06675        | 10.48382  | 6.77464   | 6.77464   | 6.90500   | 6.77464   | 6.90500   | 6.90500   |
| $V_m$ (eV)                             | -5.69317  | -3.68716  | -21.81195  | -21.41040  | -5.05575  | -4.47110  | -4.73877  | -16.26957       | -10.53337       | -5.24291  | -3.38732  | -3.38732  | -3.45250  | -3.38732  | -3.45250  | -3.45250  |
| $E_{\text{w}}(w)$ (eV)                 | -14.63489 | -14.63489 | 0          | 0          | -14.63489 | -14.63489 | -14.63489 | -15.56407       | -15.56407       | -14.63489 | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 |
| $\Delta E_{\text{H},\text{H}}(w)$ (eV) | -0.92918  | 0         | -3.58557   | -2.69893   | -2.69893  | -1.13379  | -1.85836  | 0               | 0               | 0         | 0         | 0         | 0         | 0         | 0         | 0         |
| $E_{\text{r}}(w)$ (eV)                 | -13.70571 | -14.63489 | 3.58557    | 2.69893    | -11.93596 | -13.50110 | -12.77653 | -15.56407       | -15.56407       | -14.63489 | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 |
| $E_{\text{r}}(w)$ (eV)                 | -31.63550 | -31.63554 | -63.27075  | -63.27074  | -31.63541 | -31.63551 | -31.63556 | -67.69451       | -49.66493       | -31.63553 | -31.63557 | -31.63557 | -31.63557 | -31.63557 | -31.63557 | -31.63557 |
| $E_{\text{r}}(w)$ (eV)                 | 0         | -1.85836  | -3.58557   | -2.69893   | -1.85836  | -1.13379  | -1.85836  | 0               | 0               | 0         | -1.85836  | -1.85836  | -1.44915  | -1.85836  | -1.44915  | -1.44915  |
| $E_{\text{r}}(w)$ (eV)                 | -31.63537 | -33.49373 | -66.85630  | -65.96966  | -33.49373 | -32.76916 | -33.49373 | -67.69450       | -49.66493       | -31.63557 | -33.49373 | -33.49373 | -33.49373 | -33.49373 | -33.49373 | -33.49373 |
| $\omega$ ( $10^{15}$ rad/s)            | 26.0575   | 23.3291   | 60.9581    | 59.4034    | 12.7926   | 21.4555   | 22.7749   | 24.9786         | 24.2751         | 24.1759   | 9.43699   | 9.43699   | 15.4846   | 9.43699   | 15.4846   | 15.4846   |
| $E_{\text{r}}(w)$ (eV)                 | 17.15150  | 15.35563  | 40.12366   | 39.10034   | 8.42030   | 14.12224  | 14.99085  | 16.40846        | 15.97831        | 15.91299  | 6.21159   | 6.21159   | 10.19220  | 6.21159   | 10.19220  | 10.19220  |
| $E_{\text{r}}(w)$ (eV)                 | -0.25920  | -0.25966  | -0.41891   | -0.40804   | -0.19228  | -0.24562  | -0.25655  | -0.25552        | -0.25017        | -0.24966  | -0.16515  | -0.16515  | -0.20896  | -0.16515  | -0.20896  | -0.16416  |
| $E_{\text{r}}(w)$ (eV)                 | 0.35532   | 0.10502   | 0.21747    | 0.21077    | 0.14965   | 0.11469   | 0.11618   | 0.35532         | 0.35532         | 0.35532   | 0.12312   | 0.12312   | 0.09944   | 0.12312   | 0.12312   | 0.12312   |
| $E_{\text{r}}(w)$ (eV)                 | -0.08153  | -0.20715  | -0.31017   | -0.30266   | -0.11745  | -0.18628  | -0.19921  | -0.22757        | -0.14502        | -0.07200  | -0.10359  | -0.07526  | -0.15924  | -0.10359  | -0.15924  | -0.10260  |
| $E_{\text{r}}(w)$ (eV)                 | 0.14803   | 0.14803   | 0.11441    | 0.11441    | 0.14803   | 0.14803   | 0.14803   | 0.14803         | 0.14803         | 0.14803   | 0.14803   | 0.14803   | 0.14803   | 0.14803   | 0.14803   | 0.14803   |
| $E_{\text{r}}(w)$ (eV)                 | -31.71690 | -33.70088 | -67.47664  | -66.57498  | -33.61118 | -32.95544 | -33.69294 | -67.92207       | -49.80996       | -31.70737 | -33.59732 | -33.59732 | -33.59732 | -33.59732 | -33.59732 | -33.59732 |
| $E_{\text{r}}(w)$ (eV)                 | -14.63489 | -14.63489 | -14.63489  | -14.63489  | -14.63489 | -14.63489 | -14.63489 | -14.63489       | -14.63489       | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{\text{r}}(w)$ (eV)                 | -13.59844 | 0         | 0          | 0          | 0         | 0         | 0         | -13.59844       | -13.59844       | -13.59844 | 0         | 0         | 0         | 0         | 0         | 0         |
| $E_{\text{r}}(w)$ (eV)                 | 3.48357   | 4.43110   | 8.70826    | 7.80660    | 4.34141   | 3.68566   | 4.42316   | 12.49186        | 7.83016         | 3.32601   | 4.32754   | 4.29921   | 3.97398   | 4.17951   | 3.62128   | 3.91734   |

Table 15.109. The total bond energies of alkyl carboxylic acid esters calculated using the functional group composition and the energies of Table 15.108 compared to the experimental values [3]. The magnetic energy  $E_{\text{mag}}$  that is subtracted from the weighted sum of the  $E_{\text{group}}$  ( $\text{eV}$ ) values based on composition is given by (15.57).

| Formula                                        | Name                     | C-H | C-C(O) | C=O  | C=O   | C-O | C-O   | O-C  | O-C   | O-C   | CH    | CH <sub>2</sub> | CH <sub>3</sub> | C-C | C-C | C-C | C-C | C-C | C-C | Total Bond Energy (eV) | Experiments | Relative Error |
|------------------------------------------------|--------------------------|-----|--------|------|-------|-----|-------|------|-------|-------|-------|-----------------|-----------------|-----|-----|-----|-----|-----|-----|------------------------|-------------|----------------|
| Group                                          | Group                    | (i) | Group  | (ii) | Group | (i) | Group | (ii) | Group | (iii) | Group | (i)             | Group           | (a) | (b) | (c) | (d) | (e) | (f) |                        |             |                |
| C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>   | Methyl formate           | 1   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 0               | 1               | 0   | 0   | 0   | 0   | 0   | 0   | 32.71076               | 32.762      | 0.00156        |
| C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>   | Methyl acetate           | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 0               | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 45.24849               | 45.288      | 0.00087        |
| C <sub>2</sub> H <sub>8</sub> O <sub>2</sub>   | Methyl propanoate        | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 3               | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 81.72159               | 81.726      | 0.00005        |
| C <sub>3</sub> H <sub>8</sub> O <sub>2</sub>   | Methyl butanoate         | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 4               | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 93.87929               | 93.891      | 0.00012        |
| C <sub>3</sub> H <sub>10</sub> O <sub>2</sub>  | Methyl isopropanoate     | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 5               | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 106.03699              | 106.079     | 0.00040        |
| C <sub>3</sub> H <sub>10</sub> O <sub>2</sub>  | Methyl octanoate         | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 6               | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 118.19469              | 118.217     | 0.00018        |
| C <sub>3</sub> H <sub>12</sub> O <sub>2</sub>  | Methyl decanoate         | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 7               | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 130.373                | 130.373     | 0.00016        |
| C <sub>3</sub> H <sub>14</sub> O <sub>2</sub>  | Methyl dodecanoate       | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 8               | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 142.51009              | 142.523     | 0.00009        |
| C <sub>3</sub> H <sub>16</sub> O <sub>2</sub>  | Methyl tetradecanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 9               | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 154.66779              | 154.677     | 0.00006        |
| C <sub>3</sub> H <sub>18</sub> O <sub>2</sub>  | Methyl hexadecanoate     | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 10              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 166.82549              | 166.842     | 0.00010        |
| C <sub>3</sub> H <sub>20</sub> O <sub>2</sub>  | Methyl octadecanoate     | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 11              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 178.98319              | 179.000     | 0.00009        |
| C <sub>3</sub> H <sub>22</sub> O <sub>2</sub>  | Methyl eicosanoate       | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 12              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 191.14089              | 191.170     | 0.00015        |
| C <sub>3</sub> H <sub>24</sub> O <sub>2</sub>  | Methyl pentadecanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 13              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 203.29839              | 203.336     | 0.00028        |
| C <sub>3</sub> H <sub>26</sub> O <sub>2</sub>  | Methyl heptadecanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 14              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 215.45689              | 215.488     | 0.00030        |
| C <sub>3</sub> H <sub>28</sub> O <sub>2</sub>  | Methyl nonadecanoate     | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 15              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 227.61539              | 227.647     | 0.00037        |
| C <sub>3</sub> H <sub>30</sub> O <sub>2</sub>  | Methyl undecanoate       | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 16              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 239.77389              | 239.809     | 0.00043        |
| C <sub>3</sub> H <sub>32</sub> O <sub>2</sub>  | Methyl tridecanoate      | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 17              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 251.93239              | 251.963     | 0.00049        |
| C <sub>3</sub> H <sub>34</sub> O <sub>2</sub>  | Methyl pentacosanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 18              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 264.09089              | 264.121     | 0.00055        |
| C <sub>3</sub> H <sub>36</sub> O <sub>2</sub>  | Methyl heptacosanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 19              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 276.24939              | 276.279     | 0.00061        |
| C <sub>3</sub> H <sub>38</sub> O <sub>2</sub>  | Methyl nonacosanoate     | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 20              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 288.40789              | 288.437     | 0.00067        |
| C <sub>3</sub> H <sub>40</sub> O <sub>2</sub>  | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 21              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 300.56639              | 300.596     | 0.00073        |
| C <sub>3</sub> H <sub>42</sub> O <sub>2</sub>  | Methyl hentriacontanoate | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 22              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 312.72489              | 312.754     | 0.00079        |
| C <sub>3</sub> H <sub>44</sub> O <sub>2</sub>  | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 23              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 324.88339              | 324.913     | 0.00085        |
| C <sub>3</sub> H <sub>46</sub> O <sub>2</sub>  | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 24              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 337.04189              | 337.071     | 0.00091        |
| C <sub>3</sub> H <sub>48</sub> O <sub>2</sub>  | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 25              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 349.20039              | 349.230     | 0.00097        |
| C <sub>3</sub> H <sub>50</sub> O <sub>2</sub>  | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 26              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 361.35889              | 361.388     | 0.00103        |
| C <sub>3</sub> H <sub>52</sub> O <sub>2</sub>  | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 27              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 373.51739              | 373.547     | 0.00109        |
| C <sub>3</sub> H <sub>54</sub> O <sub>2</sub>  | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 28              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 385.67589              | 385.705     | 0.00115        |
| C <sub>3</sub> H <sub>56</sub> O <sub>2</sub>  | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 29              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 397.83439              | 397.864     | 0.00121        |
| C <sub>3</sub> H <sub>58</sub> O <sub>2</sub>  | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 30              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 409.99289              | 409.999     | 0.00127        |
| C <sub>3</sub> H <sub>60</sub> O <sub>2</sub>  | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 31              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 422.15139              | 422.158     | 0.00133        |
| C <sub>3</sub> H <sub>62</sub> O <sub>2</sub>  | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 32              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 434.30989              | 434.316     | 0.00139        |
| C <sub>3</sub> H <sub>64</sub> O <sub>2</sub>  | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 33              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 446.46839              | 446.475     | 0.00145        |
| C <sub>3</sub> H <sub>66</sub> O <sub>2</sub>  | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 34              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 458.62689              | 458.633     | 0.00151        |
| C <sub>3</sub> H <sub>68</sub> O <sub>2</sub>  | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 35              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 470.78539              | 470.792     | 0.00157        |
| C <sub>3</sub> H <sub>70</sub> O <sub>2</sub>  | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 36              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 482.94389              | 482.950     | 0.00163        |
| C <sub>3</sub> H <sub>72</sub> O <sub>2</sub>  | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 37              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 495.10239              | 495.109     | 0.00169        |
| C <sub>3</sub> H <sub>74</sub> O <sub>2</sub>  | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 38              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 507.26089              | 507.267     | 0.00175        |
| C <sub>3</sub> H <sub>76</sub> O <sub>2</sub>  | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 39              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 519.41939              | 519.426     | 0.00181        |
| C <sub>3</sub> H <sub>78</sub> O <sub>2</sub>  | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 40              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 531.57789              | 531.584     | 0.00187        |
| C <sub>3</sub> H <sub>80</sub> O <sub>2</sub>  | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 41              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 543.73639              | 543.743     | 0.00193        |
| C <sub>3</sub> H <sub>82</sub> O <sub>2</sub>  | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 42              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 555.89489              | 555.901     | 0.00199        |
| C <sub>3</sub> H <sub>84</sub> O <sub>2</sub>  | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 43              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 568.05339              | 568.060     | 0.00205        |
| C <sub>3</sub> H <sub>86</sub> O <sub>2</sub>  | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 44              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 580.21189              | 580.218     | 0.00211        |
| C <sub>3</sub> H <sub>88</sub> O <sub>2</sub>  | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 45              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 592.37039              | 592.377     | 0.00217        |
| C <sub>3</sub> H <sub>90</sub> O <sub>2</sub>  | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 46              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 604.52889              | 604.535     | 0.00223        |
| C <sub>3</sub> H <sub>92</sub> O <sub>2</sub>  | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 47              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 616.68739              | 616.694     | 0.00229        |
| C <sub>3</sub> H <sub>94</sub> O <sub>2</sub>  | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 48              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 628.84589              | 628.852     | 0.00235        |
| C <sub>3</sub> H <sub>96</sub> O <sub>2</sub>  | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 49              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 641.00439              | 641.011     | 0.00241        |
| C <sub>3</sub> H <sub>98</sub> O <sub>2</sub>  | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 50              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 653.16289              | 653.169     | 0.00247        |
| C <sub>3</sub> H <sub>100</sub> O <sub>2</sub> | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 51              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 665.32139              | 665.328     | 0.00253        |
| C <sub>3</sub> H <sub>102</sub> O <sub>2</sub> | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 52              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 677.47989              | 677.486     | 0.00259        |
| C <sub>3</sub> H <sub>104</sub> O <sub>2</sub> | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 53              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 689.63839              | 689.645     | 0.00265        |
| C <sub>3</sub> H <sub>106</sub> O <sub>2</sub> | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 54              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 701.79689              | 701.803     | 0.00271        |
| C <sub>3</sub> H <sub>108</sub> O <sub>2</sub> | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 55              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 713.95539              | 713.962     | 0.00277        |
| C <sub>3</sub> H <sub>110</sub> O <sub>2</sub> | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 56              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 726.11389              | 726.120     | 0.00283        |
| C <sub>3</sub> H <sub>112</sub> O <sub>2</sub> | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 57              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 738.27239              | 738.279     | 0.00289        |
| C <sub>3</sub> H <sub>114</sub> O <sub>2</sub> | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 58              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 750.43089              | 750.437     | 0.00295        |
| C <sub>3</sub> H <sub>116</sub> O <sub>2</sub> | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 59              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 762.58939              | 762.596     | 0.00301        |
| C <sub>3</sub> H <sub>118</sub> O <sub>2</sub> | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 60              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 774.74789              | 774.754     | 0.00307        |
| C <sub>3</sub> H <sub>120</sub> O <sub>2</sub> | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 61              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 786.90639              | 786.913     | 0.00313        |
| C <sub>3</sub> H <sub>122</sub> O <sub>2</sub> | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 62              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 799.06489              | 799.071     | 0.00319        |
| C <sub>3</sub> H <sub>124</sub> O <sub>2</sub> | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 63              | 2               | 0   | 0   | 0   | 0   | 0   | 0   | 811.22339              | 811.230     | 0.00325        |
| C <sub>3</sub> H <sub>126</sub> O <sub>2</sub> | Methyl triacontanoate    | 0   | 1      | 1    | 0     | 1   | 0     | 0    | 0     | 0     | 0     | 64              | 2</             |     |     |     |     |     |     |                        |             |                |

Table 15.110. The bond angle parameters of alkyl carboxylic acid esters and experimental values [1]. In the calculation of  $\theta_r$ , the parameters from the preceding angle were used.  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{exp. AO})$ .

| Atoms of angle                                 | $2c^1$<br>Bond 1<br>( $\theta_1$ ) | $2c^2$<br>Bond 2<br>( $\theta_2$ ) | $2c^3$<br>Terminal<br>Atoms ( $\theta_3$ ) | $I_r^{\text{calculated}}$<br>Atom 1 | Atom 1<br>Hybridization<br>Designation<br>(Table 15.3.A) | $I_r^{\text{calculated}}$<br>Atom 2 | Atom 2<br>Hybridization<br>Designation<br>(Table 15.3.A) | $c_2$<br>Atom 1 | $c_2$<br>Atom 2            | $C_1$ | $C_2$ | $c_1$ | $c_2'$  | $E_r$<br>(eV) | $\theta_r$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | Cal. $\theta$<br>( $^\circ$ ) | Exp. $\theta$<br>( $^\circ$ )                                 |
|------------------------------------------------|------------------------------------|------------------------------------|--------------------------------------------|-------------------------------------|----------------------------------------------------------|-------------------------------------|----------------------------------------------------------|-----------------|----------------------------|-------|-------|-------|---------|---------------|----------------------------|----------------------------|----------------------------|-------------------------------|---------------------------------------------------------------|
| $\angle HC_1 O_1$<br>( $C^1 H$ ); $C=O$ (i)    | 2.09711                            | 2.70321                            | 3.9463                                     | -15.75493<br>$C_s$                  | 7                                                        | -13.61806                           | O                                                        | 0.86339         | 0.83395<br>(Eq. (15.11.4)) | 0.75  | 1     | 0.75  | 0.98884 | 0             |                            |                            |                            | 109.95                        | 110<br>(methyl formate)                                       |
| $\angle O_1 C_1 O_1$<br>( $C^1 H$ ); $C=O$ (i) | 2.27227                            | 2.63431                            | 4.4043                                     | -16.61853<br>$O_s$                  | 23                                                       | -16.68412<br>$O_s$                  | 25                                                       | 0.81871         | 0.81549                    | 1     | 1     | 1     | 0.81710 | -1.65376      |                            |                            |                            | 127.56                        | 127<br>(methyl formate)                                       |
| $\angle C_1 O_1 C_1$<br>( $C^1 H$ ); $C=O$ (i) | 2.70321                            | 2.63431                            | 4.4833                                     | -16.32183<br>$C_s$                  | 16                                                       | -18.47690<br>$C_s$                  | 50                                                       | 0.83360         | 0.73637                    | 1     | 1     | 1     | 0.78498 | -1.85836      |                            |                            |                            | 114.27                        | 114<br>(methyl formate)                                       |
| $\angle HC_1 H$<br>Methylene                   | 2.11106                            | 2.11106                            | 3.4252                                     | -15.75493<br>$C_s$                  | 7                                                        | H                                   | H                                                        | 0.86339         | 1                          | 1     | 1     | 0.75  | 1.15796 | 0             |                            |                            |                            | 108.44                        | 107<br>(propane)                                              |
| $\angle C_1 C_1 C_1$                           |                                    |                                    |                                            |                                     |                                                          |                                     |                                                          |                 |                            |       |       |       |         |               | 69.31                      |                            |                            | 110.49                        | 112<br>(propane)<br>113.8<br>(butane)<br>110.8<br>(isobutane) |
| $\angle C_1 C_1 H$                             |                                    |                                    |                                            |                                     |                                                          |                                     |                                                          |                 |                            |       |       |       |         |               | 69.31                      |                            |                            | 110.49                        | 111.0<br>(butane)<br>111.4<br>(isobutane)                     |
| $\angle HC_1 C_1$<br>Methyl                    | 2.09711                            | 2.09711                            | 3.4252                                     | -15.75493<br>$C_s$                  | 7                                                        | H                                   | H                                                        | 0.86339         | 1                          | 1     | 1     | 0.75  | 1.15796 | 0             |                            |                            |                            | 109.50                        | 108.5<br>(acetone)                                            |
| $\angle C_1 C_1 C_1$                           |                                    |                                    |                                            |                                     |                                                          |                                     |                                                          |                 |                            |       |       |       |         |               | 70.56                      |                            |                            | 109.44                        |                                                               |
| $\angle C_1 C_1 C_1$                           |                                    |                                    |                                            |                                     |                                                          |                                     |                                                          |                 |                            |       |       |       |         |               | 70.56                      |                            |                            | 109.44                        |                                                               |
| $\angle C_1 C_1 C_1$<br>iso $C_s$              | 2.91547                            | 2.91547                            | 4.7958                                     | -16.68412<br>$C_s$                  | 25                                                       | -16.68412<br>$C_s$                  | 25                                                       | 0.81549         | 0.81549                    | 1     | 1     | 1     | 0.81549 | -1.85836      |                            |                            |                            | 110.67                        | 110.8<br>(isobutane)                                          |
| $\angle C_1 C_1 H$<br>iso $C_s$                | 2.91547                            | 2.11323                            | 4.1633                                     | -15.55033<br>$C_s$                  | 5                                                        | -14.82575<br>$C_s$                  | 1                                                        | 0.87495         | 0.91771                    | 0.75  | 1     | 0.75  | 1.04887 | 0             |                            |                            |                            | 110.76                        |                                                               |
| $\angle C_1 C_1 H$<br>iso $C_s$                | 2.91547                            | 2.09711                            | 4.1633                                     | -15.55033<br>$C_s$                  | 5                                                        | -14.82575<br>$C_s$                  | 1                                                        | 0.87495         | 0.91771                    | 0.75  | 1     | 0.75  | 1.04887 | 0             |                            |                            |                            | 111.27                        | 111.4<br>(isobutane)                                          |
| $\angle C_1 C_1 C_1$<br>tert $C_s$             | 2.90327                            | 2.90327                            | 4.7958                                     | -15.55033<br>$C_s$                  | 5                                                        | -14.82575<br>$C_s$                  | 1                                                        | 0.87495         | 0.91771                    | 0.75  | 1     | 0.75  | 1.04887 | -1.85836      |                            |                            |                            | 111.27                        | 111.4<br>(isobutane)                                          |
| $\angle C_1 C_1 C_1$                           |                                    |                                    |                                            |                                     |                                                          |                                     |                                                          |                 |                            |       |       |       |         |               | 72.50                      |                            |                            | 107.50                        |                                                               |

# AMIDES ( $C_nH_{2n+1}NO$ , $n = 1, 2, 3, 4, 5 \dots \infty$ )

The alkyl amides,  $C_nH_{2n+1}NO$ , comprise a  $C=O$  functional group, and the single bond of carbon to the carbonyl carbon atom,  $C-C(O)$ , is also a functional group. Formamide has a  $HC=O$  moiety that comprises a more stable  $C=O$  functional group and a  $CH$  functional group that is equivalent to that of the  $CH$  (i) of aldehydes given in the corresponding section. It is also equivalent to that of the iso- $CH$  group of branched-chain-alkyl portion of the alkyl amide except that  $E_{mag}$  (Eq. (15.58)) is not subtracted from  $E_D(Group)$ . All amides further comprise a  $C-NH_2$  moiety that comprises a  $NH_2$  functional group and two types of  $C-N$  functional groups, one for formamide and the other for alkyl amides ( $RC(O)NH_2$  where  $R$  is alkyl). The alkyl portion of the alkyl amide may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in amides are equivalent to those in branched-chain alkanes.

The  $NH_2$  functional group was solved in the Dihydrogen Nitride ( $NH_2$ ) section except that the energy of the  $N-H$  MO is matched to the nitrogen-atom contribution to  $\Delta E_{H_2MO}(AO/HO)$  and  $E_r(atom-atom,msp^3.AO)$  of the  $C-N$  group. Both alkyl amide  $C=O$  groups and the  $C-C(O)$  group are equivalent to those given in the Carboxylic Acid Esters section except that  $\bar{E}_{Kvib}$  of the  $C-C(O)$  group is matched to that of an amide. The  $C-N$  groups are equivalent to those of alkyl amines given in the corresponding section except that the energy of the  $C-N$  MO is matched to that of the  $C=O$  group and  $\bar{E}_{Kvib}$  is that of an amide.  $\Delta E_{H_2MO}(AO/HO)$  of the  $C-N$  group is equal to  $E_r(atom-atom,msp^3.AO)$  of the alkyl  $C=O$  and  $C-N$  groups in order to match the energies of the corresponding MOs.

As in the case of primary amines, each  $C-N$  group is solved by hybridizing the  $2s$  and  $2p$  AOs of the  $C$  atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of

electrons between the  $C2sp^3$  HO and the  $N$  AO to form a MO permits each participating orbital to decrease in radius and energy. To meet the equipotential condition of the union of the  $C-N$   $H_2$ -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor  $c_2$  of Eq. (15.52) for the  $C-N$ -bond MO given by Eq. (15.114) is  $c_2(C2sp^3HO \text{ to } N) = 0.91140$ .

5  $E_T(atom - atom, msp^3.AO)$  (Eq. (15.52)) of the  $C=O$  group of alky amides and the  $C=O$  group of formamide are equivalent to those of the corresponding carboxylic acids and esters. The values given in the Carboxylic Acids section are  $-2.69893 \text{ eV}$  and  $-3.58557 \text{ eV}$ , respectively.

$E_T(atom - atom, msp^3.AO)$  of the amide  $C-C(O)$  group is the same as alkanes, 10 aldehydes, carboxylic acids, and carboxylic acid esters,  $-1.85836 \text{ eV}$ , where both energy contributions are given by Eq. (14.513). Also, as in the case of aldehydes,  $C_{1o} = 2C_1$  in Eq. (15.52).

In order to match energy throughout the chain of the amide molecule,  $E_T(atom - atom, msp^3.AO)$  of the  $C-N$ -bond MO in Eq. (15.52) due to the charge donation 15 from the  $C$  and  $N$  atoms to the MO is  $-1.65376 \text{ eV}$ . It is based on the energy match between the  $C2sp^3$  HO of the carbonyl and the primary amino group  $NH_2$ . It is given by the linear combination of  $-0.92918 \text{ eV}$  (Eq. (14.513)) which matches the contiguous  $C-C(O)$  or  $HC(O)$  group and  $-0.72457 \text{ eV}$  (Eq. (14.151)), the contribution of a primary amino group given in the Primary Amines section.

20 The symbols of the functional groups of alkyl amides are given in Table 15.111. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl amides are given in Tables 15.112, 15.113, and 15.114, respectively. The total energy of each alkyl amide given in Table 15.115 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.114 corresponding 25 to functional-group composition of the molecule. The bond angle parameters of alkyl amides determined using Eqs. (15.79-15.108) are given in Table 15.116.

Table 15.111. The symbols of functional groups of alkyl amides.

| Functional Group      | Group Symbol               |
|-----------------------|----------------------------|
| CH (formamide) group  | $C - H$ (i)                |
| C-C(O)                | $C - C(O)$                 |
| C=O (formamide)       | $C = O$ (i)                |
| C=O (alkyl amide)     | $C = O$ (ii)               |
| (O)C-N (formamide)    | $C - N$ (i)                |
| (O)C-N (alkyl amide)  | $C - N$ (ii)               |
| NH <sub>2</sub> group | NH <sub>2</sub>            |
| CH <sub>3</sub> group | $C - H$ (CH <sub>3</sub> ) |
| CH <sub>2</sub> group | $C - H$ (CH <sub>2</sub> ) |
| CH (alkyl) group      | $C - H$ (ii)               |
| CC bond (n-C)         | $C - C$ (a)                |
| CC bond (iso-C)       | $C - C$ (b)                |
| CC bond (tert-C)      | $C - C$ (c)                |
| CC (iso to iso-C)     | $C - C$ (d)                |
| CC (t to t-C)         | $C - C$ (e)                |
| CC (t to iso-C)       | $C - C$ (f)                |

Table 15.112. The geometrical bond parameters of alkyl amides and experimental values [1].

| Parameter                | C-H (i)           | C=O (i)                                        | C=O (ii)          | C-N (i)           | C-N (ii)          | NH <sub>2</sub>                        | C-H (CH <sub>2</sub> )                    | C-H (CH <sub>3</sub> )                    | C-C (a)                           | C-C (b)                           | C-C (c)                           | C-C (d)                           | C-C (e)                           | C-C (f)                           |
|--------------------------|-------------------|------------------------------------------------|-------------------|-------------------|-------------------|----------------------------------------|-------------------------------------------|-------------------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| $a$ (Å)                  | 1.07465           | 2.04740                                        | 1.290799          | 1.70920           | 1.75370           | 1.32297                                | 1.64920                                   | 1.67122                                   | 2.12499                           | 2.12499                           | 2.10725                           | 2.12499                           | 2.10725                           | 2.10725                           |
| $c'$ (Å)                 | 1.05661           | 1.43087                                        | 1.13613           | 1.30736           | 1.32427           | 0.97065                                | 1.04856                                   | 1.05553                                   | 1.45744                           | 1.45744                           | 1.45164                           | 1.45744                           | 1.45164                           | 1.45164                           |
| Bond Length<br>$2c'$ (Å) | 1.11827           | 1.51437                                        | 1.20243           | 1.38365           | 1.40155           | 1.02729                                | 1.10974                                   | 1.11713                                   | 1.54280                           | 1.54280                           | 1.53635                           | 1.54280                           | 1.53635                           | 1.53635                           |
| Exp. Bond Length<br>(Å)  | 1.125 (formamide) | 1.519 (acetamide)<br>1.520 (N-methylacetamide) | 1.212 (formamide) | 1.368 (formamide) | 1.380 (acetamide) | 1.027 (formamide)<br>1.022 (acetamide) | 1.107 (C-H propane)<br>1.117 (C-H butane) | 1.107 (C-H propane)<br>1.117 (C-H butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) |
| $h, c$ (Å)               | 1.29924           | 1.46439                                        | 0.61267           | 1.10098           | 1.14968           | 0.89894                                | 1.27295                                   | 1.29569                                   | 1.54616                           | 1.54616                           | 1.52750                           | 1.54616                           | 1.52750                           | 1.52750                           |
| $e$                      | 0.63095           | 0.69887                                        | 0.88018           | 0.76490           | 0.75513           | 0.73369                                | 0.63380                                   | 0.63159                                   | 0.68600                           | 0.68600                           | 0.68888                           | 0.68600                           | 0.68888                           | 0.68888                           |

Table 15.113. The MO to HO intercept geometrical bond parameters of alkyl amides.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{resp. } \Delta O)$ .

| Bond                                          | Atom | $E_T$<br>(eV)<br>Bond 1 | $E_T$<br>(eV)<br>Bond 2 | $E_T$<br>(eV)<br>Bond 3 | $E_T$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>( $\Delta O$ )<br>(eV) | $r_{\text{final}}$<br>( $a_0$ ) | $E_{\text{calculated}}$<br>(eV)<br>Final | $E(\text{C}2\text{sp}^2)$<br>(eV)<br>Final | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | $d_1$<br>( $a_0$ ) | $d_2$<br>( $a_0$ ) |
|-----------------------------------------------|------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------------------------------|---------------------------------|------------------------------------------|--------------------------------------------|----------------------------|----------------------------|--------------------|--------------------|
| $RC(O)N(H)-H$<br>( $C=O$ (i) and (ii))        | N    | -0.82688                | 0                       | 0                       | 0                       | -15.63263                                       | 0.93084                         | -15.63263                                |                                            | 66.10                      | 62.13                      | 0.61843            | 0.33222            |
| $HC(O)-NH_2$<br>( $C=O$ (i))                  | N    | -0.82688                | 0                       | 0                       | 0                       | -15.63263                                       | 0.93084                         | -15.63263                                |                                            | 76.07                      | 50.02                      | 1.09814            | 0.20922            |
| $HC(O)-NH_2$<br>( $C-N$ (i))                  | C    | -0.82688                | -1.79278                | 0                       | 0                       | -15.23535                                       | 0.91771                         | -17.44541                                | -17.25455                                  | 83.19                      | 44.70                      | 1.21492            | 0.09244            |
| $RH_2C_2C_2(O)-NH_2$<br>( $C=O$ (ii))         | N    | -0.82688                | 0                       | 0                       | 0                       | -15.63263                                       | 0.93084                         | -15.63263                                |                                            | 79.86                      | 48.10                      | 1.17127            | 0.15300            |
| $RH_2C_2C_2(O)-NH_2$<br>( $C-N$ (ii))         | C    | -0.82688                | -1.34946                | -0.92918                | 0                       | -15.472121                                      | 0.91771                         | -17.93127                                | -17.74041                                  | 89.49                      | 41.30                      | 1.31755            | 0.00672            |
| $HC_2NH_2=O$<br>( $C=O$ (i))                  | O    | -1.79278                | 0                       | 0                       | 0                       | -15.23535                                       | 1.00000                         | -16.61853                                |                                            | 42.90                      | 65.45                      | 0.53635            | 0.59978            |
| $HC_2NH_2=O$<br>( $C=O$ (ii))                 | C    | -1.79278                | -0.82688                | 0                       | 0                       | -15.472121                                      | 0.91771                         | -17.44541                                | -17.25455                                  | 44.56                      | 63.28                      | 0.58044            | 0.55569            |
| $RC_2H_2C_2(NH_2)=O$<br>( $C=O$ (i))          | O    | -1.34946                | 0                       | 0                       | 0                       | -15.23535                                       | 1.00000                         | -16.17521                                |                                            | 42.73                      | 66.31                      | 0.52193            | 0.61784            |
| $RC_2H_2C_2(NH_2)=O$<br>( $C=O$ (ii))         | C    | -1.34946                | -0.82688                | -0.92918                | 0                       | -15.472121                                      | 0.91771                         | -17.93127                                | -17.74041                                  | 46.33                      | 61.70                      | 0.61582            | 0.52395            |
| $H-C(O)NH_2$<br>( $CH$ (i))                   | C    | -1.79278                | -0.82688                | 0                       | 0                       | -15.472121                                      | 0.91771                         | -17.44541                                | -17.25455                                  | 117.61                     | 32.13                      | 1.41810            | 0.36148            |
| $RH_2C_2-C_2(O)NH_2$<br>( $C_2$ )             | C    | -0.92918                | -1.34946                | -0.82688                | 0                       | -15.472121                                      | 0.91771                         | -17.93127                                | -17.74041                                  | 122.98                     | 25.76                      | 1.84386            | 0.47299            |
| $H_2C_2-C_2(O)NH_2$<br>( $C_2$ )              | C    | -0.92918                | 0                       | 0                       | 0                       | -15.254487                                      | 0.91771                         | -15.75493                                | -15.56407                                  | 107.73                     | 34.17                      | 1.69388            | 0.26301            |
| $RH_2C_2H_2C_2-C_2(O)NH_2$<br>( $C-C$ (i))    | C    | -0.92918                | -0.92918                | 0                       | 0                       | -15.347405                                      | 0.91771                         | -16.68411                                | -16.49325                                  | 114.01                     | 30.58                      | 1.76270            | 0.33183            |
| $C-C(H)(CH_2)$<br>( $C-C$ (ii))               | C    | -0.92918                | 0                       | 0                       | 0                       | -15.254487                                      | 0.91771                         | -15.75493                                | -15.56407                                  | 102.51                     | 41.48                      | 1.23564            | 0.18708            |
| $C-C(H)(CH_2)$<br>( $C-C$ (iii))              | C    | -0.92918                | -0.92918                | 0                       | 0                       | -15.347406                                      | 0.91771                         | -16.68412                                | -16.49325                                  | 111.53                     | 35.84                      | 1.33486            | 0.29933            |
| $H_2C_2-C_2H_2CH_2-$<br>( $C-C$ (iv))         | C    | -0.92918                | -0.92918                | -0.92918                | 0                       | -15.440324                                      | 0.91771                         | -17.61330                                | -17.42244                                  | 118.90                     | 31.37                      | 1.42988            | 0.37336            |
| $H_2C_2-C_2H_2CH_2-$<br>( $C-C$ (v))          | C    | -0.92918                | 0                       | 0                       | 0                       | -15.254487                                      | 0.91771                         | -15.75493                                | -15.56407                                  | 116.18                     | 30.08                      | 1.83879            | 0.38106            |
| $R-H_2C_2(H_2C_2-R)HCH_2-$<br>( $C-C$ (vi))   | C    | -0.92918                | -0.92918                | -0.92918                | 0                       | -15.347406                                      | 0.91771                         | -16.68412                                | -16.49325                                  | 123.59                     | 26.06                      | 1.50890            | 0.45117            |
| $R-H_2C_2(H_2C_2-R)HCH_2-$<br>( $C-C$ (vii))  | C    | -0.92918                | -0.92918                | -0.92918                | 0                       | -15.440324                                      | 0.91771                         | -17.61330                                | -17.42244                                  | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| $R-H_2C_2(H_2C_2-R)HCH_2-$<br>( $C-C$ (viii)) | C    | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -15.411860                                      | 0.91771                         | -17.92866                                | -17.73779                                  | 131.79                     | 21.74                      | 1.95734            | 0.50570            |
| $isoC_2C_2(H_2C_2-R)HCH_2-$<br>( $C-C$ (ix))  | C    | -0.92918                | -0.92918                | -0.92918                | 0                       | -15.440324                                      | 0.91771                         | -17.61330                                | -17.42244                                  | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| $isoC_2C_2(H_2C_2-R)HCH_2-$<br>( $C-C$ (x))   | C    | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -15.411860                                      | 0.91771                         | -17.92866                                | -17.73779                                  | 129.96                     | 22.66                      | 1.94462            | 0.49298            |
| $isoC_2C_2(H_2C_2-R)HCH_2-$<br>( $C-C$ (xi))  | C    | -0.72457                | -0.92918                | -0.92918                | 0                       | -15.411860                                      | 0.91771                         | -17.40869                                | -17.21783                                  | 127.22                     | 24.04                      | 1.92443            | 0.47279            |
| $isoC_2C_2(H_2C_2-R)HCH_2-$<br>( $C-C$ (xii)) | C    | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -15.411860                                      | 0.91771                         | -17.92866                                | -17.73779                                  | 129.96                     | 22.66                      | 1.94462            | 0.49298            |



Table 15.114. The energy parameters (eV) of functional groups of alkyl amides.

| Parameters                        | C-H (i)   | C-C(O)    | C=O (i)    | C-N (i)   | NH <sub>2</sub> | CH <sub>2</sub> | CH <sub>3</sub> | C-H (ii)  | C-C (a)   | C-C (b)   | C-C (c)   | C-C (d)   | C-C (e)   | C-C (f)   | C-C (g)   |
|-----------------------------------|-----------|-----------|------------|-----------|-----------------|-----------------|-----------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| $\eta_1$                          | 1         | 1         | 2          | 1         | 2               | 3               | 3               | 1         | 1         | 1         | 1         | 1         | 1         | 1         | 1         |
| $\eta_2$                          | 0         | 0         | 0          | 0         | 0               | 2               | 2               | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 0         |
| $\eta_3$                          | 0         | 0         | 0          | 0         | 1               | 0               | 0               | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 0         |
| $\zeta_1$                         | 0.75      | 0.5       | 0.5        | 0.5       | 0.75            | 0.75            | 0.75            | 0.75      | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       |
| $\zeta_2$                         | 1         | 1         | 1          | 1         | 0.93613         | 1               | 1               | 1         | 1         | 1         | 1         | 1         | 1         | 1         | 1         |
| $\zeta_3$                         | 1         | 1         | 1          | 1         | 0.75            | 1               | 1               | 1         | 1         | 1         | 1         | 1         | 1         | 1         | 1         |
| $\zeta_4$                         | 0.91771   | 0.91771   | 0.85395    | 0.91140   | 1               | 0.91771         | 0.91771         | 0.91771   | 0.91771   | 0.91771   | 0.91771   | 0.91771   | 0.91771   | 0.91771   | 0.91771   |
| $\zeta_5$                         | 0         | 0         | 2          | 0         | 0               | 0               | 0               | 1         | 0         | 0         | 0         | 1         | 0         | 1         | 0         |
| $\zeta_6$                         | 1         | 2         | 4          | 2         | 1               | 1               | 1               | 1         | 2         | 2         | 2         | 2         | 2         | 2         | 2         |
| $\zeta_7$                         | 1         | 0         | 0          | 0         | 2               | 3               | 2               | 1         | 0         | 0         | 0         | 0         | 0         | 0         | 0         |
| $\zeta_8$                         | 0.75      | 1         | 0.5        | 0.5       | 1.5             | 0.75            | 0.75            | 0.75      | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       |
| $\zeta_9$                         | 1         | 1         | 1          | 1         | 1               | 1               | 1               | 1         | 1         | 1         | 1         | 1         | 1         | 1         | 1         |
| $\zeta_{10}$                      | -35.12015 | -30.19634 | -112.61934 | -38.24008 | -36.88558       | -78.77719       | -107.32728      | -70.41425 | -28.79214 | -28.79214 | -28.79214 | -28.79214 | -28.79214 | -28.79214 | -28.79214 |
| $\zeta_{11}$                      | 12.87680  | 9.50874   | 23.95107   | 10.40705  | 10.27417        | 28.03446        | 38.92728        | 25.78002  | 9.33352   | 9.33352   | 9.33352   | 9.33352   | 9.33352   | 9.33352   | 9.33352   |
| $\zeta_{12}$                      | 10.48382  | 7.37432   | 43.62389   | 42.82081  | 11.18655        | 29.77286        | 32.53914        | 21.06675  | 6.77464   | 6.77464   | 6.77464   | 6.77464   | 6.77464   | 6.77464   | 6.77464   |
| $\zeta_{13}$                      | -5.24291  | -3.68716  | -21.81195  | -5.59327  | -5.23825        | -14.88643       | -16.26957       | -10.33337 | -3.38732  | -3.38732  | -3.38732  | -3.38732  | -3.38732  | -3.38732  | -3.38732  |
| $\zeta_{14}$                      | -14.63489 | -14.63489 | 0          | -14.63489 | -14.63489       | -14.53414       | -15.56407       | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 |
| $\Delta E_{1,10}$ (eV)            | 0         | 0         | -3.58557   | -2.69893  | -5.23932        | -4.32268        | -1.65376        | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 0         |
| $\Delta E_{1,10}$ (eV)            | -14.63489 | -14.63489 | 3.58557    | 2.69893   | -9.39557        | -10.28221       | -12.88038       | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 |
| $\Delta E_{1,10}$ (eV)            | 0         | 0         | 0          | 0         | 0               | 0               | -14.53414       | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 0         |
| $\Delta E_{1,10}$ (eV)            | -31.63553 | -31.63553 | -63.27075  | -31.63553 | -31.63553       | -67.69451       | -49.66493       | -31.63553 | -31.63553 | -31.63553 | -31.63553 | -31.63553 | -31.63553 | -31.63553 | -31.63553 |
| $\Delta E_{1,10}$ (eV)            | 0         | -1.83836  | -5.58557   | -2.69893  | -1.65376        | -1.65376        | 0               | 0         | -1.83836  | -1.83836  | -1.44915  | -1.83836  | -1.44915  | -1.83836  | -1.44915  |
| $\Delta E_{1,10}$ (eV)            | -31.63557 | -33.49373 | -66.85630  | -65.90606 | -33.28912       | -33.28912       | -48.73660       | -49.66493 | -33.49373 | -33.49373 | -33.49373 | -33.49373 | -33.49373 | -33.49373 | -33.49373 |
| $\omega$ (10 <sup>15</sup> rad/s) | 24.1759   | 14.1117   | 60.9581    | 59.4034   | 13.0822         | 12.5874         | 24.2751         | 24.1759   | 9.43699   | 9.43699   | 15.4846   | 9.43699   | 15.4846   | 9.43699   | 15.4846   |
| $\bar{\nu}_{1,10}$ (eV)           | 15.01299  | 9.28860   | 40.12366   | 39.10034  | 8.61093         | 8.28256         | 39.10250        | 15.97831  | 6.21159   | 6.21159   | 10.19220  | 6.21159   | 10.19220  | 6.21159   | 10.19220  |
| $\bar{\nu}_{1,10}$ (eV)           | -0.24966  | -0.20195  | -0.41891   | -0.40804  | -0.19325        | -0.18957        | -0.39136        | -0.25017  | -0.16515  | -0.16515  | -0.20896  | -0.16515  | -0.20896  | -0.16515  | -0.20896  |
| $\bar{\nu}_{1,10}$ (eV)           | 0.35532   | 0.14655   | 0.21747    | 0.21077   | 0.17358         | 0.17358         | 0.40929         | 0.35532   | 0.12312   | 0.12312   | 0.09944   | 0.12312   | 0.09944   | 0.12312   | 0.09944   |
| $\bar{\nu}_{1,10}$ (eV)           | (13.4588) | (13.4588) | (13.4588)  | (13.4588) | (13.4588)       | (13.4588)       | (13.4588)       | (13.4588) | (13.4588) | (13.4588) | (13.4588) | (13.4588) | (13.4588) | (13.4588) | (13.4588) |
| $\bar{\nu}_{1,10}$ (eV)           | -0.07200  | -0.12867  | -0.31017   | -0.30266  | -0.10647        | -0.10278        | -0.18672        | -0.14502  | -0.07200  | -0.07200  | -0.15924  | -0.07200  | -0.15924  | -0.07200  | -0.15924  |
| $\bar{\nu}_{1,10}$ (eV)           | 0.14803   | 0.14803   | 0.14441    | 0.14441   | 0.14803         | 0.14803         | 0.14803         | 0.14803   | 0.14803   | 0.14803   | 0.14803   | 0.14803   | 0.14803   | 0.14803   | 0.14803   |
| $\bar{\nu}_{1,10}$ (eV)           | -31.70737 | -33.62241 | -67.47664  | -66.57498 | -33.39559       | -33.39559       | -49.11003       | -49.80996 | -33.59732 | -33.59732 | -33.59732 | -33.59732 | -33.59732 | -33.59732 | -33.59732 |
| $\bar{\nu}_{1,10}$ (eV)           | -14.63489 | -14.63489 | -14.63489  | -14.63489 | -14.63489       | -14.63489       | -14.53414       | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $\bar{\nu}_{1,10}$ (eV)           | -13.59844 | 0         | 0          | 0         | 0               | 0               | -13.59844       | -13.59844 | 0         | 0         | 0         | 0         | 0         | 0         | 0         |
| $\bar{\nu}_{1,10}$ (eV)           | 3.47404   | 4.35263   | 8.70826    | 7.80660   | 4.12581         | 4.12212         | 7.57901         | 7.80616   | 4.32754   | 4.29921   | 3.97598   | 4.17951   | 3.97598   | 4.17951   | 3.97598   |
| $\bar{\nu}_{1,10}$ (eV)           |           |           |            |           |                 |                 |                 |           |           |           |           |           |           |           |           |

Table 15.115. The total bond energies of alkyl amides calculated using the functional group composition and the energies of Table 15.114 compared to the experimental values [3].

| Formula            | Name                    | C-H (i) | C-C(O) | C=O (i) | C=O (ii) | C-N (i) | C-N (ii) | NH <sub>2</sub> | CH <sub>3</sub> | CH <sub>2</sub> | CH (ii) | C-C (a) | C-C (b) | C-C (c) | C-C (d) | C-C (e) | C-C (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|--------------------|-------------------------|---------|--------|---------|----------|---------|----------|-----------------|-----------------|-----------------|---------|---------|---------|---------|---------|---------|---------|-----------------------------------|-------------------------------------|----------------|
| CH <sub>3</sub> NO | Formamide               | 1       | 0      | 1       | 0        | 1       | 0        | 1               | 0               | 0               | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 22.69712                          | 22.697                              | 0.00041        |
| CH <sub>3</sub> NO | Acetamide               | 0       | 1      | 0       | 0        | 1       | 0        | 1               | 1               | 0               | 0       | 1       | 0       | 0       | 0       | 0       | 0       | 36.13222                          | 36.103                              | -0.00135       |
| CH <sub>3</sub> NO | Propanamide             | 0       | 1      | 0       | 0        | 1       | 0        | 1               | 1               | 1               | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 48.30992                          | 48.264                              | -0.00094       |
| CH <sub>3</sub> NO | Butanamide              | 0       | 1      | 0       | 0        | 1       | 0        | 1               | 2               | 0               | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 60.46762                          | 60.449                              | -0.00030       |
| CH <sub>3</sub> NO | 2-Methylpropanamide     | 0       | 1      | 0       | 0        | 1       | 0        | 1               | 2               | 0               | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 60.46762                          | 60.449                              | -0.00030       |
| CH <sub>3</sub> NO | Pentanamide             | 0       | 1      | 0       | 0        | 1       | 0        | 1               | 3               | 0               | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 60.51509                          | 60.455                              | -0.00090       |
| CH <sub>3</sub> NO | 2,2-Dimethylpropanamide | 0       | 1      | 0       | 0        | 1       | 0        | 1               | 3               | 0               | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 72.63232                          | 72.481                              | -0.00200       |
| CH <sub>3</sub> NO | Hexanamide              | 0       | 1      | 0       | 0        | 1       | 0        | 1               | 4               | 0               | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 72.67890                          | 72.718                              | 0.00054        |
| CH <sub>3</sub> NO | Heptanamide             | 0       | 1      | 0       | 0        | 1       | 0        | 1               | 5               | 0               | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 84.78302                          | 84.780                              | -0.00004       |
| CH <sub>3</sub> NO | Octanamide              | 0       | 1      | 0       | 0        | 1       | 0        | 1               | 6               | 0               | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 109.09842                         | 109.071                             | -0.00075       |

Table 15.116. The bond angle parameters of alkyl amides and experimental values [1]. In the calculation of  $\theta_i$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{exp}, \text{AO})$ .

| Atoms of Angle                                                                                      | $2c^1$<br>Bond 1<br>( $a_1$ ) | $2c^2$<br>Bond 2<br>( $a_2$ ) | $2c^3$<br>Terminal<br>Atom ( $a_3$ ) | $V_{\text{residual}}$<br>Atom 1 | Atom 1<br>Hybridization<br>Designation<br>(Table 15.3.A) | $E_{\text{residual}}$<br>Atom 2 | Atom 2<br>Hybridization<br>Designation<br>(Table 15.3.A) | $c_2$<br>Atom 1          | $c_1$<br>Atom 2           | $C_1$ | $C_2$ | $\zeta_1$ | $\zeta_2$ | $E_T$<br>(eV) | $\theta_i$<br>( $^\circ$ ) | $\theta_j$<br>( $^\circ$ ) | $\theta_k$<br>( $^\circ$ ) | Cal. $\theta$<br>( $^\circ$ ) | Exp. $\theta$<br>( $^\circ$ )                                                      |
|-----------------------------------------------------------------------------------------------------|-------------------------------|-------------------------------|--------------------------------------|---------------------------------|----------------------------------------------------------|---------------------------------|----------------------------------------------------------|--------------------------|---------------------------|-------|-------|-----------|-----------|---------------|----------------------------|----------------------------|----------------------------|-------------------------------|------------------------------------------------------------------------------------|
| $\angle \text{HNH}$                                                                                 | 1.94130                       | 1.94130                       | 3.1464                               | -14.33414<br>$N$                | N                                                        | H                               | H                                                        | 0.93613<br>(Eq. (15.62)) | 1                         | 1     | 1     | 0.75      | 1.06823   | 0             |                            |                            |                            | 108.27                        |                                                                                    |
| $\angle \text{C}^{\text{H}} \text{NH}$<br>( $\text{C}^{\text{H}}$ (i); $\text{C}_n = \text{O}$ (i)) | 2.61473                       | 1.94130                       | 3.9328                               | -14.33414<br>$N$                | N                                                        | $\text{C}_n$                    | 1                                                        | 0.93613<br>(Eq. (15.62)) | 0.91771                   | 0.75  | 1     | 0.75      | 0.98053   | 0             |                            |                            |                            | 118.61                        | 119.2<br>(formamide)                                                               |
| $\angle \text{HC}^{\text{H}} \text{N}$<br>( $\text{CH}$ (i); $\text{C}_n = \text{O}$ (i))           | 2.11323                       | 2.61473                       | 4.0825                               | -14.82575<br>$\text{C}_n$       | 1                                                        | $N$                             | N                                                        | 0.91771                  | 0.93613<br>(Eq. (15.62))  | 0.75  | 1     | 0.75      | 1.02006   | 0             |                            |                            |                            | 119.04                        |                                                                                    |
| $\angle \text{HC}^{\text{H}} \text{O}$<br>( $\text{CH}$ (i))                                        | 2.11323                       | 2.27227                       | 3.7238                               | -14.82575<br>$\text{C}_n$       | 1                                                        | $\text{O}$                      | O                                                        | 0.91771                  | 0.83395<br>(Eq. (15.114)) | 0.75  | 1     | 0.75      | 0.93052   | 0             |                            |                            |                            | 116.18                        |                                                                                    |
| $\angle \text{OC}^{\text{H}} \text{N}$<br>( $\text{C}_n = \text{O}$ (i))                            | 2.27227                       | 2.61473                       | 4.3359                               | 16.17521<br>$\text{O}$          | 12                                                       | $N$                             | 17                                                       | 0.84115                  | 0.83078                   | 1     | 1     | 1         | 0.83596   | -1.44915      |                            |                            |                            | 124.91                        | 125.0<br>(formamide)                                                               |
| $\angle \text{C}^{\text{H}} \text{C}^{\text{H}} \text{N}$<br>( $\text{C}_n = \text{O}$ (iii))       | 2.86175                       | 2.64855                       | 4.6904                               | -15.75493<br>$\text{C}_n$       | 7                                                        | $N$                             | N                                                        | 0.86359                  | 0.91140<br>(Eq. (15.116)) | 1     | 1     | 1         | 0.8749    | -1.44915      |                            |                            |                            | 116.63                        | 115.1<br>(acetamide)                                                               |
| $\angle \text{C}^{\text{H}} \text{C}^{\text{H}} \text{O}$<br>( $\text{C}_n = \text{O}$ (iii))       | 2.86175                       | 2.27954                       | 4.5007                               | -16.68411<br>$\text{O}$         | 24                                                       | $\text{O}$                      | O                                                        | 0.81549                  | 0.83595<br>(Eq. (15.114)) | 1     | 1     | 1         | 0.83472   | -1.63376      |                            |                            |                            | 124.63                        |                                                                                    |
| $\angle \text{OC}^{\text{H}} \text{N}$<br>( $\text{C}_n = \text{O}$ (iii))                          | 2.27954                       | 2.64855                       | 4.3126                               | 16.17521<br>$\text{O}$          | 12                                                       | $N$                             | 17                                                       | 0.84115                  | 0.83078                   | 1     | 1     | 1         | 0.83596   | -1.44915      |                            |                            |                            | 121.95                        | 122.0<br>(acetamide)                                                               |
| $\angle \text{HC}^{\text{H}} \text{H}$                                                              | 2.11106                       | 2.11106                       | 3.4252                               | -15.75493                       | 7                                                        | H                               | H                                                        | 0.86359                  | 1                         | 1     | 1     | 0.75      | 1.15796   | 0             |                            |                            |                            | 108.44                        | 107<br>(propane)                                                                   |
| $\angle \text{C}^{\text{H}} \text{C}^{\text{H}} \text{C}^{\text{H}}$                                |                               |                               |                                      |                                 |                                                          |                                 |                                                          |                          |                           |       |       |           |           |               | 69.51                      |                            |                            | 110.49                        | 113.8<br>(butane)<br>110.8<br>(acetone)<br>111.0<br>(butane)<br>111.4<br>(acetone) |
| $\angle \text{C}^{\text{H}} \text{C}^{\text{H}} \text{H}$                                           |                               |                               |                                      |                                 |                                                          |                                 |                                                          |                          |                           |       |       |           |           |               | 69.51                      |                            |                            | 110.49                        | 108.5<br>(acetone)                                                                 |
| $\angle \text{HC}^{\text{H}} \text{H}$                                                              | 2.09711                       | 2.09711                       | 3.4252                               | -15.75493                       | 7                                                        | H                               | H                                                        | 0.86359                  | 1                         | 1     | 1     | 0.75      | 1.15796   | 0             |                            |                            |                            | 109.44                        |                                                                                    |
| $\angle \text{C}^{\text{H}} \text{C}^{\text{H}} \text{C}^{\text{H}}$                                |                               |                               |                                      |                                 |                                                          |                                 |                                                          |                          |                           |       |       |           |           |               | 70.56                      |                            |                            | 109.44                        |                                                                                    |
| $\angle \text{C}^{\text{H}} \text{C}^{\text{H}} \text{H}$                                           |                               |                               |                                      |                                 |                                                          |                                 |                                                          |                          |                           |       |       |           |           |               | 70.56                      |                            |                            | 109.44                        |                                                                                    |
| $\angle \text{C}^{\text{H}} \text{C}^{\text{H}} \text{C}^{\text{H}}$<br>iso $\text{C}_n$            | 2.91547                       | 2.91547                       | 4.7958                               | -16.68412<br>$\text{C}_n$       | 25                                                       | $\text{C}_n$                    | 25                                                       | 0.81549                  | 0.81549                   | 1     | 1     | 1         | 0.81549   | -1.85856      |                            |                            |                            | 110.67                        | 110.8<br>(isobutane)                                                               |
| $\angle \text{C}^{\text{H}} \text{C}^{\text{H}} \text{H}$<br>iso $\text{C}_n$                       | 2.91547                       | 2.11323                       | 4.1633                               | -15.35033<br>$\text{C}_n$       | 5                                                        | $\text{C}_n$                    | 1                                                        | 0.87495                  | 0.91771                   | 0.75  | 1     | 0.75      | 1.04887   | 0             |                            |                            |                            | 110.76                        |                                                                                    |
| $\angle \text{C}^{\text{H}} \text{C}^{\text{H}} \text{H}$<br>iso $\text{C}_n$                       | 2.91547                       | 2.09711                       | 4.1633                               | -15.55033<br>$\text{C}_n$       | 5                                                        | $\text{C}_n$                    | 1                                                        | 0.87495                  | 0.91771                   | 0.75  | 1     | 0.75      | 1.04887   | 0             |                            |                            |                            | 111.27                        | 111.4<br>(isobutane)                                                               |
| $\angle \text{C}^{\text{H}} \text{C}^{\text{H}} \text{C}^{\text{H}}$<br>iso $\text{C}_n$            | 2.90327                       | 2.90327                       | 4.7958                               | -15.55033<br>$\text{C}_n$       | 5                                                        | $\text{C}_n$                    | 1                                                        | 0.87495                  | 0.91771                   | 0.75  | 1     | 0.75      | 1.04887   | -1.85856      |                            |                            |                            | 111.27                        | 111.4<br>(isobutane)                                                               |
| $\angle \text{C}^{\text{H}} \text{C}^{\text{H}} \text{C}^{\text{H}}$                                |                               |                               |                                      |                                 |                                                          |                                 |                                                          |                          |                           |       |       |           |           |               | 72.50                      |                            |                            | 107.50                        |                                                                                    |

# N-ALKYL AND N,N-DIALKYL-AMIDES ( $C_nH_{2n+1}NO$ , $n = 2, 3, 4, 5 \dots \infty$ )

The N-alkyl and N,N-dialkyl amides,  $C_nH_{2n+1}NO$ , comprise a  $C=O$  functional group, and the single bond of carbon to the carbonyl carbon atom,  $C-C(O)$ , is also a functional group. Formamide has a  $HC=O$  moiety that comprises a more stable  $C=O$  functional group and a  
 5  $CH$  functional group that is equivalent to that of the iso- $CH$  group of branched-chain-alkyl portion of the N-alkyl or N,N-dialkyl amide. All amides further comprise a  $C-N(R_1)R_2$  moiety that comprises two types of  $C-N$  functional groups, one for formamide and the other for alkyl amides ( $RC(O)N(R_1)R_2$  where  $R$  is alkyl). The N or N,N-dialkyl moiety comprises three additional groups depending on the alkyl substitution of the nitrogen. In the case of a  
 10 single methyl or alkyl substitution, the  $NH-C$  bond and  $NH$  are functional groups, and the  $N-C$  bond of a di-substituted nitrogen is the third.

The alkyl portion of the N-alkyl or N,N-dialkyl amide may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds.  
 15 The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in N-alkyl or  
 20 N,N-dialkyl amides are equivalent to those in branched-chain alkanes.

The  $NH$  functional group was solved in the Hydrogen Nitride ( $NH$ ) section except that the energy of the  $N-H$  MO is matched to the nitrogen-atom contribution to  $\Delta E_{H_2MO}(AO/HO)$  and  $E_r(atom-atom, msp^3.AO)$  of the  $C-N$  group. The  $C-C(O)$  group, both N-alkyl or N,N-dialkyl amide  $C=O$  groups, and both  $C-N$  groups are equivalent to those given in the  
 25 Amides section.

As in the case of primary amines, each  $N-C$  group is solved by hybridizing the  $2s$  and  $2p$  AOs of the  $C$  atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the  $N$  AO to form a MO permits each participating orbital to decrease in radius and energy. To meet the equipotential condition of the union of the

$N-C$   $H_2$ -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor  $c_2$  of Eq. (15.52) for the  $N-C$ -bond MO given by Eq. (15.114) is  $c_2(C2sp^3HO \text{ to } N) = 0.91140$ .

$E_r(atom - atom, msp^3.AO)$  of the N-substituted amide  $C-C(O)$  group is the same as alkanes, aldehydes, carboxylic acids, carboxylic acid esters, and amides,  $-1.85836 \text{ eV}$ , where  
 5 both energy contributions are given by Eq. (14.513). Also, as in the case of aldehydes,  $C_{1o} = 2C_1$  in Eq. (15.52).

$E_r(atom - atom, msp^3.AO)$  (Eq. (15.52)) of the  $C=O$  group of N-substituted alky amides and the  $C=O$  group of N-substituted formamide are equivalent to those of the corresponding carboxylic acids, carboxylic esters, and amides. The values given in the  
 10 Carboxylic Acids section are  $-2.69893 \text{ eV}$  and  $-3.58557 \text{ eV}$ , respectively.

$E_r(atom - atom, msp^3.AO)$  of both  $C-N$  functional groups are the same as those of the corresponding groups of amides,  $-1.65376 \text{ eV}$ .  $E_r(atom - atom, msp^3.AO)$  of the singly-substituted  $NH-C$ -bond MO in Eq. (15.52) due to the charge donation from the  $N$  and  $C$  atoms to the MO is  $-0.92918 \text{ eV}$ . It is equivalent to that of tertiary amines and matches the  
 15 energy of the  $NH-C$  group to that of the  $C-N$  group wherein  $E_r(atom - atom, msp^3.AO)$  of the latter is a linear combination of  $-0.92918 \text{ eV}$  (Eq. (14.513)) and  $-0.72457 \text{ eV}$  (Eq. (14.151)).  $E_r(atom - atom, msp^3.AO)$  of the doubly-substituted  $N-C$ -bond MO is  $-0.72457 \text{ eV}$ . It is equivalent to that of the contribution of each atom of a primary amine and also matches the energy of the  $N-C$  group to that of the  $C-N$  group by matching one of the  
 20 components of  $E_r(atom - atom, msp^3.AO)$  of the latter.

The symbols of the functional groups of N-alkyl and N,N-dialkyl amides are given in Table 15.117. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of N-alkyl and N,N-dialkyl amides are given in Tables 15.118, 15.119, and 15.120, respectively. The total energy of each N-alkyl  
 25 or N,N-dialkyl amide given in Table 15.121 was calculated as the sum over the integer multiple of each  $E_p(group)$  of Table 15.120 corresponding to functional-group composition of the molecule. The bond angle parameters of N-alkyl and N,N-dialkyl amides determined using Eqs. (15.79-15.108) are given in Table 15.122.

Table 15.117. The symbols of functional groups of N-alkyl and N,N-dialkyl amides.

| Functional Group                           | Group Symbol               |
|--------------------------------------------|----------------------------|
| C-C(O)                                     | $C - C(O)$                 |
| C=O (N-alkyl and N,N-dialkyl formamide)    | $C = O$ (i)                |
| C=O (N-alkyl and N,N-dialkyl amide)        | $C = O$ (ii)               |
| (O)C-N (N-alkyl and N,N-dialkyl formamide) | $C - N$ (i)                |
| (O)C-N (N-alkyl and N,N-dialkyl amide)     | $C - N$ (ii)               |
| NH group                                   | $NH$                       |
| N-C (N-alkyl)                              | $N - C$ (i)                |
| N-C (N,N,-dialkyl)                         | $N - C$ (ii)               |
| CH <sub>3</sub> group                      | $C - H$ (CH <sub>3</sub> ) |
| CH <sub>2</sub> group                      | $C - H$ (CH <sub>2</sub> ) |
| CH (alkyl) group                           | $C - H$                    |
| CC bond (n-C)                              | $C - C$ (a)                |
| CC bond (iso-C)                            | $C - C$ (b)                |
| CC bond (tert-C)                           | $C - C$ (c)                |
| CC (iso to iso-C)                          | $C - C$ (d)                |
| CC (t to t-C)                              | $C - C$ (e)                |
| CC (t to iso-C)                            | $C - C$ (f)                |

Table 15.118. The geometrical bond parameters of N-alkyl and N,N-dialkyl amides and experimental values [1]

| Parameter            | C-C (f)                   | C-C (g)           | C-C (h)                   | C-N (i)           | C-N (j)           | NH      | N-C (k)                   | N-C (l) | C-H (CH <sub>1</sub> ) | C-H (CH <sub>2</sub> ) | C-H (CH <sub>3</sub> ) | C-C (a)         | C-C (b)         | C-C (c)        | C-C (d)         | C-C (e)        | C-C (f)         |
|----------------------|---------------------------|-------------------|---------------------------|-------------------|-------------------|---------|---------------------------|---------|------------------------|------------------------|------------------------|-----------------|-----------------|----------------|-----------------|----------------|-----------------|
| $a$ (Å)              | 2.04740                   | 1.200799          | 1.29907                   | 1.70920           | 1.75370           | 1.28620 | 1.96313                   | 1.97794 | 1.64920                | 1.67122                | 1.67465                | 2.12499         | 2.12499         | 2.10725        | 2.12499         | 2.10725        | 2.10725         |
| $c'$ (Å)             | 1.43087                   | 1.13613           | 1.13977                   | 1.30726           | 1.32427           | 0.95706 | 1.40112                   | 1.40639 | 1.04856                | 1.05533                | 1.05661                | 1.45744         | 1.45744         | 1.45164        | 1.45744         | 1.45164        | 1.45164         |
| Bond Length          | 1.51437                   | 1.20243           | 1.20628                   | 1.38365           | 1.40155           | 1.01291 | 1.48288                   | 1.48846 | 1.10974                | 1.11713                | 1.11827                | 1.54280         | 1.54280         | 1.53635        | 1.54280         | 1.53635        | 1.53635         |
| $2c'$ (Å)            |                           |                   |                           |                   |                   |         |                           |         |                        |                        |                        |                 |                 |                |                 |                |                 |
| Exp. Bond Length (Å) | 1.520 (N-methylacetamide) | 1.212 (formamide) | 1.225 (N-methylacetamide) | 1.368 (formamide) | 1.380 (acetamide) |         | 1.469 (N-methylacetamide) |         | 1.107 (C-H propane)    | 1.107 (C-H propane)    | 1.122 (isobutane)      | 1.532 (propane) | 1.532 (propane) | 1.531 (butane) | 1.532 (propane) | 1.531 (butane) | 1.532 (propane) |
| $b, c$ (Å)           | 1.46439                   | 0.61267           | 0.62331                   | 1.10098           | 1.14968           | 0.85927 | 1.37505                   | 1.39079 | 1.27295                | 1.29569                | 1.29924                | 1.54616         | 1.54616         | 1.52750        | 1.54616         | 1.52750        | 1.52750         |
| $\sigma$             | 0.69887                   | 0.88018           | 0.87737                   | 0.76490           | 0.75513           | 0.74410 | 0.71372                   | 0.71104 | 0.63580                | 0.63159                | 0.62095                | 0.68600         | 0.68600         | 0.68888        | 0.68600         | 0.68888        | 0.68888         |

Table 15.119. The MO to HO intercept geometrical bond parameters of N-alkyl and N,N-dialkyl amides.  $R, R', R''$  are H, methyl, or alkyl groups.  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{moy}, \text{AO})$ .

| Bond                                                                                       | Atom           | $E_r$<br>(eV)<br>Bond 1 | $E_r$<br>(eV)<br>Bond 2 | $E_r$<br>(eV)<br>Bond 3 | $E_r$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>(eV) | $r_{\text{bond}}$<br>( $a_0$ ) | $r_{\text{atom}}$<br>( $a_0$ ) | $E(\text{C}2\text{sp}^2)$<br>(eV)<br>Final | $\theta'$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | $d_1$<br>( $a_0$ ) | $d_2$<br>( $a_0$ ) |
|--------------------------------------------------------------------------------------------|----------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------------|--------------------------------|--------------------------------|--------------------------------------------|---------------------------|----------------------------|----------------------------|--------------------|--------------------|
| $R'C_2(O)N(C_2H_5)-H$<br>(C=O (i) and (ii))<br>(C-N (i) and (ii))                          | N              | -0.82688                | -0.46459                | 0                       | 0                       |                               | 0.93084                        | 0.84418                        | -16.11722                                  | 115.47                    | 64.53                      | 62.49                      | 0.59403            | 0.36303            |
| $R'C_2(O)N(H)-C_2H_5$<br>(C=O (i) and (ii))<br>(C-N (i) and (ii))<br>(N-C (i))             | N              | -0.82688                | -0.46459                | 0                       | 0                       |                               | 0.93084                        | 0.84418                        | -16.11722                                  | 78.61                     | 101.39                     | 37.00                      | 1.50779            | 0.16667            |
| $R'C_2(O)N(H)-C_2H_5$<br>(C=O (i) and (ii))<br>(C-N (i) and (ii))<br>(N-C (i))             | C <sub>s</sub> | -0.46459                | 0                       | 0                       | 0                       | -151.08028                    | 0.91771                        | 0.88983                        | -15.26034                                  | 83.37                     | 96.63                      | 40.00                      | 1.50383            | 0.10271            |
| $R'C_2(O)N(H)-C_2H_5$<br>(C=O (i) and (ii))<br>(C-N (i) and (ii))<br>(N-C (i))             | N              | -0.82688                | -0.46459                | 0                       | 0                       |                               | 0.93084                        | 0.84418                        | -16.11722                                  | 78.61                     | 101.39                     | 37.00                      | 1.50779            | 0.16667            |
| $R'C_2(O)N(H)-C_2H_5$<br>(C=O (i) and (ii))<br>(C-N (i) and (ii))<br>(N-C (i))             | C <sub>s</sub> | -0.46459                | -0.92918                | 0                       | 0                       | -151.00946                    | 0.91771                        | 0.83885                        | -16.21952                                  | 78.02                     | 101.39                     | 36.64                      | 1.57525            | 0.17413            |
| $R'C_2(O)N(C_2H_5)-C_2H_5$<br>(C=O (i) and (ii))<br>(C-N (i) and (ii))<br>(N-C (i))        | N              | -0.82688                | -0.36229                | -0.36229                | 0                       |                               | 0.93084                        | 0.83078                        | -16.37720                                  | 75.57                     | 104.43                     | 35.35                      | 1.61336            | 0.20697            |
| $R'C_2(O)N(C_2H_5)-C_2H_5$<br>(C=O (i) and (ii))<br>(C-N (i) and (ii))<br>(N-C (i))        | C <sub>s</sub> | -0.36229                | 0                       | 0                       | 0                       | -151.07798                    | 0.91771                        | 0.89582                        | -15.18804                                  | 82.59                     | 97.41                      | 39.70                      | 1.52188            | 0.11549            |
| $R'C_2(O)N(C_2H_5C_2H_4R)-C_2H_5$<br>(C=O (i) and (ii))<br>(C-N (i) and (ii))<br>(N-C (i)) | N              | -0.82688                | -0.36229                | -0.36229                | 0                       |                               | 0.93084                        | 0.83078                        | -16.37720                                  | 75.57                     | 104.43                     | 35.35                      | 1.61336            | 0.20697            |
| $R'C_2(O)N(C_2H_5C_2H_4R)-C_2H_5$<br>(C=O (i) and (ii))<br>(C-N (i) and (ii))<br>(N-C (i)) | C <sub>s</sub> | -0.36229                | 0                       | 0                       | 0                       | -151.07798                    | 0.91771                        | 0.89582                        | -15.18804                                  | 82.59                     | 97.41                      | 39.70                      | 1.52188            | 0.11549            |
| $R'C_2(O)N(R')-C_2H_5C_2H_4R$<br>(C=O (i) and (ii))<br>(C-N (i) and (ii))<br>(N-C (i))     | N              | -0.82688                | -0.36229                | -0.36229                | 0                       |                               | 0.93084                        | 0.83078                        | -16.37720                                  | 75.57                     | 104.43                     | 35.35                      | 1.61336            | 0.20697            |
| $R'C_2(O)N(R')-C_2H_5C_2H_4R$<br>(C=O (i) and (ii))<br>(C-N (i) and (ii))<br>(N-C (i))     | C <sub>s</sub> | -0.36229                | -0.92918                | 0                       | 0                       | -152.90716                    | 0.91771                        | 0.84418                        | -16.11722                                  | 77.12                     | 102.88                     | 36.28                      | 1.59451            | 0.18812            |
| $HC_2(O)-N(H)R$<br>(C=O (i))<br>(C-N (i))<br>(N-C (i))<br><i>R = methyl or alkyl</i>       | N              | -0.82688                | -0.46459                | 0                       | 0                       |                               | 0.93084                        | 0.84418                        | -16.11722                                  | 102.07                    | 77.93                      | 48.57                      | 1.13000            | 0.17647            |
| $HC_2(O)-N(H)R$<br>(C=O (i))<br>(C-N (i))<br>(N-C (i))<br><i>R = methyl or alkyl</i>       | C <sub>s</sub> | -0.82688                | -1.79278                | 0                       | 0                       | -154.23535                    | 0.91771                        | 0.77991                        | -17.44541                                  | 96.81                     | 83.19                      | 44.70                      | 1.21492            | 0.09244            |
| $HC_2(O)-N(R)R$<br>(C=O (i))<br>(C-N (i))<br>(N-C (i))<br><i>R, R' = methyl or alkyl</i>   | N              | -0.82688                | -0.36229                | -0.36229                | 0                       |                               | 0.93084                        | 0.83078                        | -16.37720                                  | 101.03                    | 78.97                      | 47.79                      | 1.14842            | 0.15895            |
| $HC_2(O)-N(R)R$<br>(C=O (i))<br>(C-N (i))<br>(N-C (i))                                     | C <sub>s</sub> | -0.82688                | -1.79278                | 0                       | 0                       | -154.23535                    | 0.91771                        | 0.77991                        | -17.44541                                  | 96.81                     | 83.19                      | 44.70                      | 1.21492            | 0.09244            |

|                                                                                                                                    |                |          |          |          |          |            |         |         |           |        |        |       |         |         |
|------------------------------------------------------------------------------------------------------------------------------------|----------------|----------|----------|----------|----------|------------|---------|---------|-----------|--------|--------|-------|---------|---------|
| $R, R' = \text{methyl or alkyl}$<br>$R^1H_2C_2C_2(O)-N(H)R$<br>(C=O (6))<br>(C-N (6))<br>(N-C (6))<br>$R = \text{methyl or alkyl}$ | N              | -0.82688 | -0.4459  | 0        | 0        | 0          | 0.5084  | 0.8418  | -16.1722  | 98.16  | 81.84  | 46.62 | 1.2046  | 0.1192  |
| $R^1H_2C_2C_2(O)-N(H)R$<br>(C=O (6))<br>(C-N (6))<br>(N-C (6))<br>$R = \text{methyl or alkyl}$                                     | C <sub>s</sub> | -0.82688 | -1.34946 | -0.92918 | 0        | -154.72121 | 0.91771 | 0.75878 | -17.93127 | 90.51  | 89.49  | 41.30 | 1.3155  | 0.00672 |
| $R^1H_2C_2C_2(O)-N(R)R$<br>(C=O (6))<br>(C-N (6))<br>(N-C (6))<br>$R, R' = \text{methyl or alkyl}$                                 | N              | -0.82688 | -0.36229 | -0.36229 | 0        |            | 0.5084  | 0.8078  | -16.37720 | 97.66  | 82.94  | 45.82 | 1.2220  | 0.10207 |
| $R^1H_2C_2C_2(O)-N(R)R$<br>(C=O (6))<br>(C-N (6))<br>(N-C (6))<br>$R, R' = \text{methyl or alkyl}$                                 | C <sub>s</sub> | -0.82688 | -1.34946 | -0.92918 | 0        | -154.72121 | 0.91771 | 0.75878 | -17.93127 | 90.51  | 89.49  | 41.30 | 1.3155  | 0.00672 |
| $HC_4(N(R)R) = O$<br>(C=O (6))<br>$R, R' = H, \text{methyl, or alkyl}$                                                             | O              | -1.70278 | 0        | 0        | 0        |            | 1.00000 | 0.81871 | -16.61853 | 137.10 | 42.90  | 65.45 | 0.51655 | 0.59778 |
| $HC_4(N(R)R) = O$<br>(C=O (6))<br>$R, R' = H, \text{methyl, or alkyl}$                                                             | C <sub>s</sub> | -1.70278 | -0.82688 | 0        | 0        | -154.23535 | 0.91771 | 0.77991 | -17.44541 | 135.44 | 44.56  | 63.28 | 0.58044 | 0.55569 |
| $HC_4H_2C_2(N(R)R) = O$<br>(C=O (6))<br>$R, R' = H, \text{methyl, or alkyl}$                                                       | O              | -1.34946 | 0        | 0        | 0        |            | 1.00000 | 0.84115 | -16.17521 | 137.27 | 42.73  | 66.31 | 0.52193 | 0.61784 |
| $HC_4H_2C_2(N(R)R) = O$<br>(C=O (6))<br>$R, R' = H, \text{methyl, or alkyl}$                                                       | C <sub>s</sub> | -1.34946 | -0.82688 | -0.92918 | 0        | -154.72121 | 0.91771 | 0.75878 | -17.93127 | 133.67 | 46.33  | 61.70 | 0.61582 | 0.52595 |
| $H-C(O)N(R)R$<br>$R, R' = H, \text{methyl, or alkyl}$                                                                              | C <sub>s</sub> | -1.70278 | -0.82688 | 0        | 0        | -154.23535 | 0.91771 | 0.77991 | -17.44541 | 62.39  | 117.61 | 32.13 | 1.41810 | 0.56148 |
| $RH_2C_2-C_2(O)N(R)R$<br>$R, R' = H, \text{methyl, or alkyl}$                                                                      | C <sub>s</sub> | -0.92918 | -1.34946 | -0.82688 | 0        | -154.72121 | 0.91771 | 0.75878 | -17.93127 | 57.02  | 122.98 | 25.76 | 1.84586 | 0.41599 |
| $H_2C_2-C_2(O)N(R)R$<br>$R, R' = H, \text{methyl, or alkyl}$                                                                       | C <sub>s</sub> | -0.92918 | 0        | 0        | 0        | -152.54487 | 0.91771 | 0.86359 | -15.75493 | 72.27  | 107.73 | 34.17 | 1.69388 | 0.36301 |
| $RH_2C_2H_2C_2-C_2(O)N(R)R$<br>$R, R' = H, \text{methyl, or alkyl}$                                                                | C <sub>s</sub> | -0.92918 | -0.92918 | 0        | 0        | -153.47405 | 0.91771 | 0.81549 | -16.68411 | 65.99  | 114.01 | 30.58 | 1.76270 | 0.33183 |
| $C-H(CH_3)$<br>$C-H(CH_3)$                                                                                                         | C <sub>s</sub> | -0.92918 | 0        | 0        | 0        | -152.54487 | 0.91771 | 0.86359 | -15.75493 | 77.49  | 102.51 | 41.48 | 1.2564  | 0.18708 |
| $C-H(CH_3)$<br>$C-H(CH_3)$                                                                                                         | C <sub>s</sub> | -0.92918 | -0.92918 | 0        | 0        | -153.47405 | 0.91771 | 0.81549 | -16.68412 | 68.47  | 111.53 | 35.84 | 1.35486 | 0.29933 |
| $H_2C_2H_2CH_2-$<br>$(C-C(6))$                                                                                                     | C <sub>s</sub> | -0.92918 | 0        | 0        | 0        | -154.40324 | 0.91771 | 0.77247 | -17.61330 | 61.10  | 118.90 | 31.37 | 1.42988 | 0.37326 |
| $H_2C_2H_2CH_2-$<br>$(C-C(6))$                                                                                                     | C <sub>s</sub> | -0.92918 | -0.92918 | 0        | 0        | -152.54487 | 0.91771 | 0.86359 | -15.75493 | 63.82  | 116.18 | 30.08 | 1.83879 | 0.38106 |
| $R-H_2C_2C_2(H_2C_2-R)HC(H_2)-$<br>$(C-C(6))$                                                                                      | C <sub>s</sub> | -0.92918 | -0.92918 | 0        | 0        | -153.47406 | 0.91771 | 0.81549 | -16.68412 | 56.41  | 123.59 | 26.06 | 1.90890 | 0.45117 |
| $R-H_2C_2C_2(R-H_2C_2)C_2(R'-H_2C_2)CH_2-$<br>$(C-C(6))$                                                                           | C <sub>s</sub> | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.40324 | 0.91771 | 0.77247 | -17.61330 | 48.30  | 131.70 | 21.90 | 1.97162 | 0.51388 |
| $HOOC_4C_2(H_2C_2-R)HC(H_2)-$<br>$(C-C(6))$                                                                                        | C <sub>s</sub> | -0.92918 | -0.92918 | -0.92918 | 0        | -154.40324 | 0.91771 | 0.75869 | -17.93666 | 48.21  | 131.79 | 21.74 | 1.95734 | 0.50570 |
| $HOOC_4(R'-H_2C_2)C_2(R-H_2C_2)CH_2-$<br>$(C-C(6))$                                                                                | C <sub>s</sub> | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.31399 | 0.91771 | 0.76765 | -17.92866 | 50.04  | 129.96 | 22.66 | 1.94462 | 0.49298 |
| $HOOC_4C_2(H_2C_2-R)HC(H_2)-$<br>$(C-C(6))$                                                                                        | C <sub>s</sub> | -0.92918 | -0.92918 | -0.92918 | 0        | -154.19863 | 0.91771 | 0.76155 | -17.48609 | 52.78  | 127.22 | 24.04 | 1.92443 | 0.47279 |
| $HOOC_4(R'-H_2C_2)C_2(R-H_2C_2)CH_2-$<br>$(C-C(6))$                                                                                | C <sub>s</sub> | -0.92918 | -0.72457 | -0.72457 | -0.72457 | -154.31399 | 0.91771 | 0.76765 | -17.92866 | 50.04  | 129.96 | 22.66 | 1.94462 | 0.49298 |



Table 15.120. The energy parameters (eV) of functional groups of N-alkyl and N,N-dialkyl amides.

| Parameters                                      | C-C (V)<br>Group | C=O (f)<br>Group | C-N (f)<br>Group | NH<br>Group | N-C (f)<br>Group | CH <sub>3</sub><br>Group | CH <sub>2</sub><br>Group | C-H<br>Group | C-C (a)<br>Group | C-C (b)<br>Group | C-C (c)<br>Group | C-C (d)<br>Group | C-C (e)<br>Group | C-C (f)<br>Group |
|-------------------------------------------------|------------------|------------------|------------------|-------------|------------------|--------------------------|--------------------------|--------------|------------------|------------------|------------------|------------------|------------------|------------------|
| $\mu_1$                                         | 1                | 2                | 1                | 1           | 1                | 3                        | 2                        | 1            | 1                | 1                | 1                | 1                | 1                | 1                |
| $\mu_2$                                         | 0                | 0                | 0                | 0           | 0                | 2                        | 1                        | 0            | 0                | 0                | 0                | 0                | 0                | 0                |
| $\mu_3$                                         | 0                | 0                | 0                | 0           | 0                | 0                        | 0                        | 0            | 0                | 0                | 0                | 0                | 0                | 0                |
| $C_1$                                           | 0.5              | 0.5              | 0.5              | 0.5         | 0.5              | 0.75                     | 0.75                     | 0.75         | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              |
| $C_2$                                           | 1                | 1                | 1                | 1           | 1                | 1                        | 1                        | 1            | 1                | 1                | 1                | 1                | 1                | 1                |
| $C_3$                                           | 1                | 1                | 1                | 1           | 1                | 1                        | 1                        | 1            | 1                | 1                | 1                | 1                | 1                | 1                |
| $C_4$                                           | 0.91771          | 0.85395          | 0.91140          | 1           | 0.91140          | 0.91771                  | 0.91771                  | 0.91771      | 0.91771          | 0.91771          | 0.91771          | 0.91771          | 0.91771          | 0.91771          |
| $C_5$                                           | 0                | 2                | 0                | 1           | 0                | 0                        | 1                        | 1            | 0                | 0                | 0                | 1                | 1                | 0                |
| $C_6$                                           | 2                | 4                | 2                | 1           | 2                | 1                        | 1                        | 1            | 2                | 2                | 2                | 2                | 2                | 2                |
| $C_7$                                           | 0                | 0                | 0                | 1           | 0                | 3                        | 2                        | 1            | 0                | 0                | 0                | 0                | 0                | 0                |
| $C_8$                                           | 1                | 0.5              | 0.5              | 0.5         | 0.5              | 0.75                     | 0.75                     | 0.75         | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              |
| $C_{20}$                                        | 1                | 1                | 1                | 1           | 1                | 1                        | 1                        | 1            | 1                | 1                | 1                | 1                | 1                | 1                |
| $I_1$ (eV)                                      | -30.19634        | -112.61934       | -111.25473       | -36.88538   | -31.67393        | -107.32728               | -70.41425                | -35.12015    | -28.79214        | -28.79214        | -29.10112        | -29.10112        | -29.10112        | -29.10112        |
| $I_2$ (eV)                                      | 9.50874          | 23.95107         | 23.87467         | 10.47075    | 9.70679          | 38.92728                 | 25.78002                 | 12.87680     | 9.33352          | 9.33352          | 9.33352          | 9.33352          | 9.33352          | 9.33352          |
| $I_3$ (eV)                                      | 7.3432           | 43.62389         | 42.82081         | 11.18655    | 10.51650         | 7.92833                  | 32.53914                 | 21.06675     | 6.77464          | 6.77464          | 6.90500          | 6.74664          | 6.90500          | 6.90500          |
| $I_4$ (eV)                                      | -3.68716         | -21.81195        | -21.41040        | -5.59327    | -5.5825          | -7.9482                  | -10.53337                | -5.24291     | -3.38732         | -3.38732         | -3.45250         | -3.38732         | -3.45250         | -3.45250         |
| $E_{1,100}^{\text{calc}}(\text{eV})$            | -14.63489        | 0                | -14.63489        | -14.63489   | -14.63489        | -15.56407                | -15.56407                | -14.63489    | -15.56407        | -15.56407        | -15.56407        | -15.56407        | -15.56407        | -15.56407        |
| $\Delta E_{1,100}^{\text{calc}}(\text{eV})$     | 0                | -3.88257         | -2.69893         | -3.5268     | -0.92918         | -0.72457                 | 0                        | 0            | 0                | 0                | 0                | 0                | 0                | 0                |
| $E_{2,100}^{\text{calc}}(\text{eV})$            | -14.63489        | 3.8857           | 2.69893          | -10.28221   | -13.70571        | -13.91032                | -15.56407                | -14.63489    | -15.56407        | -15.56407        | -15.56407        | -15.56407        | -15.56407        | -15.56407        |
| $I_5$ (eV)                                      | -31.65334        | -63.27075        | -63.27074        | -31.65337   | -31.65337        | -67.69451                | -49.66493                | -31.65337    | -31.65337        | -31.65337        | -31.65337        | -31.65337        | -31.65337        | -31.65337        |
| $I_6$ (eV)                                      | -1.85836         | -3.8857          | -2.69893         | -1.65376    | -0.92918         | -0.72457                 | 0                        | 0            | -1.85836         | -1.85836         | -1.44915         | -1.85836         | -1.44915         | -1.44915         |
| $I_7$ (eV)                                      | -33.49373        | -66.85630        | -65.96966        | -33.28912   | -32.55994        | -67.69450                | -49.66493                | -31.65337    | -33.49373        | -33.49373        | -33.49373        | -33.49373        | -33.49373        | -33.49373        |
| $\omega$ (10 <sup>3</sup> rad s <sup>-1</sup> ) | 14.1117          | 60.9581          | 59.4034          | 13.0822     | 12.5874          | 44.9494                  | 24.2751                  | 24.1759      | 9.43699          | 9.43699          | 15.4846          | 9.43699          | 9.55643          | 9.55643          |
| $E_8$ (eV)                                      | 9.28860          | 40.12566         | 39.10034         | 8.28526     | 6.9543           | 16.40846                 | 15.97831                 | 15.91299     | 6.21159          | 6.21159          | 10.19220         | 6.21159          | 6.29021          | 6.29021          |
| $\bar{E}_9$ (eV)                                | -0.20195         | -0.41891         | -0.40804         | -0.19325    | -0.17039         | -0.16837                 | -0.23532                 | -0.25017     | -0.16515         | -0.16515         | -0.20896         | -0.16515         | -0.16416         | -0.16416         |
| $E_{10,000}^{\text{calc}}(\text{eV})$           | 0.14655          | 0.21747          | 0.17358          | 0.40696     | 0.12944          | 0.35532                  | 0.35532                  | 0.35532      | 0.12312          | 0.12312          | 0.09944          | 0.12312          | 0.12312          | 0.12312          |
| $E_{11,000}^{\text{calc}}(\text{eV})$           | -0.12867         | -0.31017         | -0.30266         | -0.10647    | -0.10567         | -0.10365                 | -0.22757                 | -0.14502     | -0.10359         | -0.10359         | -0.15924         | -0.10359         | -0.10260         | -0.10260         |
| $E_{12,000}^{\text{calc}}(\text{eV})$           | 0.14803          | 0.11441          | 0.11441          | 0.14803     | 0.14803          | 0.14803                  | 0.14803                  | 0.14803      | 0.14803          | 0.14803          | 0.14803          | 0.14803          | 0.14803          | 0.14803          |
| $E_{13,000}^{\text{calc}}(\text{eV})$           | -33.62241        | -67.47664        | -66.57498        | -33.39190   | -32.67022        | -67.92207                | -49.80996                | -31.70737    | -33.59732        | -33.59732        | -33.59732        | -33.59732        | -33.59732        | -33.59732        |
| $E_{14,000}^{\text{calc}}(\text{eV})$           | -14.63489        | -14.63489        | -14.63489        | -14.63489   | -14.63489        | -14.63489                | -14.63489                | -14.63489    | -14.63489        | -14.63489        | -14.63489        | -14.63489        | -14.63489        | -14.63489        |
| $E_{15,000}^{\text{calc}}(\text{eV})$           | 0                | 0                | 0                | 0           | 0                | 0                        | -13.59844                | -13.59844    | 0                | 0                | 0                | 0                | 0                | 0                |
| $E_{16,000}^{\text{calc}}(\text{eV})$           | 4.5263           | 8.70826          | 7.80660          | 4.12581     | 3.40044          | 12.49186                 | 7.83016                  | 3.32601      | 4.32754          | 4.32754          | 3.97398          | 4.17951          | 3.62128          | 3.91734          |

Table 15.121. The total bond energies of N-alkyl and N,N-dialkyl amides calculated using the functional group composition and the energies of Table 15.120 compared to the experimental values [3].

| Formula  | Name                  | C=O (f)<br>Group | C-N (f)<br>Group | NH<br>Group | N-C (f)<br>Group | CH <sub>3</sub><br>Group | CH <sub>2</sub><br>Group | C-H<br>Group | C-C (a)<br>Group | C-C (b)<br>Group | C-C (c)<br>Group | C-C (d)<br>Group | C-C (e)<br>Group | C-C (f)<br>Group | Calculated<br>Total Bond<br>Energy<br>(eV) | Experimental<br>Total Bond<br>Energy<br>(eV) | Relative<br>Error |
|----------|-----------------------|------------------|------------------|-------------|------------------|--------------------------|--------------------------|--------------|------------------|------------------|------------------|------------------|------------------|------------------|--------------------------------------------|----------------------------------------------|-------------------|
| C14H29NO | N,N-Dimethylformamide | 0                | 1                | 0           | 0                | 0                        | 0                        | 1            | 0                | 0                | 0                | 0                | 0                | 0                | 41.5142                                    | 41.5142                                      | 0.0000            |
| C14H29NO | N,N-Dimethylacetamide | 0                | 0                | 1           | 0                | 2                        | 0                        | 0            | 0                | 0                | 0                | 0                | 0                | 0                | 50.3142                                    | 50.3142                                      | -0.0001           |
| C14H29NO | N-Ethylacetamide      | 1                | 0                | 1           | 0                | 1                        | 3                        | 0            | 0                | 0                | 0                | 0                | 0                | 0                | 84.6349                                    | 84.6349                                      | -0.0005           |



UREA ( $CH_4N_2O$ )

Urea,  $CH_4N_2O$ , comprises a  $C=O$  functional group and two  $C-NH_2$  moieties that each comprise a  $NH_2$  functional group and a  $C-N$  functional group. The  $C=O$  group is equivalent to that given for formamide in the Amides section except that the energy terms due to oscillation in the transition state are matched to that of urea. The  $NH_2$  and  $C-N$  functional groups are also equivalent to those given in the Amides section.  $E_r(atom-atom,msp^3.AO)$  (Eq. (15.52)) of the  $C=O$  and  $C-N$  groups are equivalent to those of formamide. The values given in the Amides section are  $-3.58557\text{ eV}$ , and  $-1.65376\text{ eV}$ , respectively.

The symbols of the functional groups of urea are given in Table 15.123. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of urea are given in Tables 15.124, 15.125, and 15.126, respectively. The total energy of urea given in Table 15.127 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.126 corresponding to functional-group composition of the molecule. The bond angle parameters of urea determined using Eqs. (15.79-15.108) are given in Table 15.128.

Table 15.123. The symbols of functional groups of urea.

| Functional Group | Group Symbol |
|------------------|--------------|
| $C=O$ (urea)     | $C=O$        |
| $(O)C-N$ (urea)  | $C-N$        |
| $NH_2$ group     | $NH_2$       |

Table 15.124. The geometrical bond parameters of urea and experimental values [1].

| Parameter                             | C=O<br>Group         | C-N<br>Group         | NH <sub>2</sub><br>Group                     |
|---------------------------------------|----------------------|----------------------|----------------------------------------------|
| $a$ ( $a_0$ )                         | 1.290799             | 1.70920              | 1.32297                                      |
| $c'$ ( $a_0$ )                        | 1.13613              | 1.30736              | 0.97065                                      |
| Bond Length<br>$2c'$ ( $\text{\AA}$ ) | 1.20243              | 1.38365              | 1.02729                                      |
| Exp. Bond Length<br>( $\text{\AA}$ )  | 1.212<br>(formamide) | 1.368<br>(formamide) | 1.027<br>(formamide)<br>1.022<br>(acetamide) |
| $b_1 c'$ ( $a_0$ )                    | 0.61267              | 1.10098              | 0.89894                                      |
| $c$                                   | 0.88018              | 0.76490              | 0.73369                                      |

Table 15.125. The MO to HO intercept geometrical bond parameters of urea.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{exp}^3, \text{AO})$ .

| Bond              | Atom | $E_T$<br>(eV)<br>Bond 1 | $E_T$<br>(eV)<br>Bond 2 | $E_T$<br>(eV)<br>Bond 3 | $E_T$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>C2,sp <sup>3</sup><br>(eV) | $r_{\text{final}}$<br>( $a_0$ ) | $E_{\text{Coulomb}}$<br>(eV)<br>Final | $E(\text{C2,sp}^3)$<br>(eV)<br>Final | $\theta'$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | $d_1$<br>( $a_0$ ) | $d_2$<br>( $a_0$ ) |
|-------------------|------|-------------------------|-------------------------|-------------------------|-------------------------|-----------------------------------------------------|---------------------------------|---------------------------------------|--------------------------------------|---------------------------|----------------------------|----------------------------|--------------------|--------------------|
| $H_1NC(O)N(H)-H$  | N    | -0.82688                | 0                       | 0                       | 0                       |                                                     | 0.93084                         | -15.65263                             |                                      | 113.90                    | 66.10                      | 62.13                      | 0.61843            | 0.5222             |
| $H_1NC(O)-NH_2$   | N    | -0.82688                | 0                       | 0                       | 0                       |                                                     | 0.93084                         | -15.65263                             |                                      | 103.93                    | 76.07                      | 50.02                      | 1.09814            | 0.20922            |
| $H_1NC(O)-NH_2$   | C    | -0.82688                | -1.79278                | -0.82688                | 0                       | -155.06223                                          | 0.91771                         | -18.27229                             | -18.08143                            | 93.56                     | 86.44                      | 42.45                      | 1.26106            | 0.04630            |
| $H_1NC(NH_2)=O$   | O    | -1.79278                | 0                       | 0                       | 0                       |                                                     | 1.00000                         | -16.61853                             |                                      | 137.10                    | 42.90                      | 63.45                      | 0.53635            | 0.59978            |
| $H_1NC_2(NH_2)=O$ | C    | -1.79278                | -0.82688                | -0.82688                | 0                       | -155.06223                                          | 0.91771                         | -18.27229                             | -18.08143                            | 133.82                    | 46.18                      | 61.27                      | 0.62034            | 0.51559            |

Table 15.126. The energy parameters (eV) of functional groups of urea.

| Parameters                                                     | C = O<br>Group  | C - N<br>Group  | NH <sub>2</sub><br>Group |
|----------------------------------------------------------------|-----------------|-----------------|--------------------------|
| $n_1$                                                          | 2               | 1               | 2                        |
| $n_2$                                                          | 0               | 0               | 0                        |
| $n_3$                                                          | 0               | 0               | 1                        |
| $C_1$                                                          | 0.5             | 0.5             | 0.75                     |
| $C_2$                                                          | 1               | 1               | 0.93613                  |
| $c_1$                                                          | 1               | 1               | 0.75                     |
| $c_2$                                                          | 0.85395         | 0.91140         | 1                        |
| $c_3$                                                          | 2               | 0               | 0                        |
| $c_4$                                                          | 4               | 2               | 1                        |
| $c_5$                                                          | 0               | 0               | 2                        |
| $C_{1w}$                                                       | 0.5             | 0.5             | 1.5                      |
| $C_{2w}$                                                       | 1               | 1               | 1                        |
| $V_e$ (eV)                                                     | -112.61934      | -38.24008       | -78.77719                |
| $V_p$ (eV)                                                     | 23.95107        | 10.40705        | 28.03446                 |
| $T$ (eV)                                                       | 43.62389        | 11.18655        | 29.77286                 |
| $V_m$ (eV)                                                     | -21.81195       | -5.59327        | -14.88643                |
| $E(\text{AO} \text{HO})$ (eV)                                  | 0               | -14.63489       | -14.53414                |
| $\Delta E_{H_2MO}(\text{AO} \text{HO})$ (eV)                   | -3.58557        | -5.23932        | -1.65376                 |
| $E_r(\text{AO} \text{HO})$ (eV)                                | 3.58557         | -9.39557        | -12.88038                |
| $E(n, \text{AO} \text{HO})$ (eV)                               | 0               | 0               | -14.53414                |
| $E_r(H_2MO)$ (eV)                                              | -63.27075       | -31.63533       | -48.73668                |
| $E_r(\text{atom} - \text{atom}, \text{msp}^3, \text{AO})$ (eV) | -3.58557        | -1.65376        | 0                        |
| $E_r(MO)$ (eV)                                                 | -66.85630       | -33.28912       | -48.73660                |
| $\omega$ ( $10^{15}$ rad / s)                                  | 19.9334         | 13.0822         | 59.4067                  |
| $E_K$ (eV)                                                     | 13.12053        | 8.61093         | 39.10250                 |
| $\bar{E}_D$ (eV)                                               | -0.23955        | -0.19325        | -0.39136                 |
| $\bar{E}_{Kvib}$ (eV)                                          | 0.21747<br>[32] | 0.17358<br>[33] | 0.40929<br>[22]          |
| $\bar{E}_{osc}$ (eV)                                           | -0.13081        | -0.10647        | -0.18672                 |
| $E_{moq}$ (eV)                                                 | 0.11441         | 0.14803         | 0.14185                  |
| $E_r(\text{Group})$ (eV)                                       | -67.11793       | -33.39559       | -49.11003                |
| $E_{total}(c_1 \text{AO} \text{HO})$ (eV)                      | -14.63489       | -14.63489       | -14.53414                |
| $E_{total}(c_2 \text{AO} \text{HO})$ (eV)                      | 0               | 0               | -13.59844                |
| $E_D(\text{Group})$ (eV)                                       | 8.34955         | 4.12581         | 7.37901                  |

Table 15.127. The total bond energies of urea calculated using the functional group composition and the energies of Table 15.126 compared to the experimental values [3].

| Formula                          | Name | C = O<br>Group | C - N<br>Group | NH <sub>2</sub><br>Group | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|----------------------------------|------|----------------|----------------|--------------------------|-----------------------------------------|-------------------------------------------|----------------|
| CH <sub>4</sub> N <sub>2</sub> O | Urea | 1              | 2              | 2                        | 31.35919                                | 31.393                                    | 0.00108        |

Table 15.128. The bond angle parameters of urea and experimental values [1]. In the calculation of  $\theta_v$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(atom - atom, msp, AO)$ .

| Angles of Angle | $2c'$<br>Bond 1<br>( $a_v$ ) | $2c'$<br>Bond 2<br>( $a_v$ ) | $2c'$<br>Terminal<br>Atom ( $a_v$ ) | $E_T$<br>Terminal<br>Atom 1 | Atom 1<br>Hybridization<br>Designation<br>(Table 15.3.A) | $c_2$<br>Atom 1          | $c_2$<br>Atom 2 | $C_1$  | $C_2$ | $c_1$ | $c'_2$  | $E_T$<br>(eV) | $\theta_v$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | Cal. $\theta$<br>( $^\circ$ ) | Exp. $\theta$<br>( $^\circ$ ) |
|-----------------|------------------------------|------------------------------|-------------------------------------|-----------------------------|----------------------------------------------------------|--------------------------|-----------------|--------|-------|-------|---------|---------------|----------------------------|----------------------------|----------------------------|-------------------------------|-------------------------------|
| $\angle HNH$    | 1.94130                      | 1.94130                      | 3.1464                              | -14.53414                   | N                                                        | 0.93613<br>Eq. (15.62)   | H               | 1      | 1     | 0.75  | 1.06823 | 0             |                            |                            |                            | 108.27                        |                               |
| $\angle C'NH$   | 2.61473                      | 1.94130                      | 3.9328                              | -14.53414                   | N                                                        | 0.93613<br>(Eq. (15.62)) | C'              | 0.7171 | 1     | 0.75  | 0.98033 | 0             |                            |                            |                            | 118.61                        | 119.2<br>(formamide)          |
| $\angle OC'N$   | 2.27227                      | 2.61473                      | 4.3359                              | 16.17521                    | 12                                                       | 0.84115                  | N               | 1      | 1     | 1     | 0.83596 | -1.44915      |                            |                            |                            | 124.91                        | 125.0<br>(formamide)          |

# CARBOXYLIC ACID HALIDES ( $C_nH_{2n-1}OX$ , $X = F, Cl, Br, I$ ; $n = 1, 2, 3, 4, 5 \dots \infty$ )

The alkyl carboxylic acid halides,  $C_nH_{2n-1}OX$ , comprise a  $C=O$  functional group, and the single bond of carbon to the carbonyl carbon atom,  $C-C(O)$ , is also a functional group. All carboxylic acid halides further comprise a  $C-X$  functional group where  $X$  is a halogen atom. The alkyl portion of the alkyl carboxylic acid halide may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acids are equivalent to those in branched-chain alkanes.

The alkyl carboxylic acid halide  $C=O$  and  $C-C(O)$  groups are equivalent to those given in the Aldehydes section and the Ketones section, respectively. The values of  $E_r(atom-atom,msp^3.AO)$  given in these sections are  $-2.69893 eV$  and  $-1.44915 eV$ , respectively.

As in the case of alkyl halides, each  $(O)C-X$  group is solved by hybridizing the  $2s$  and  $2p$  AOs of the  $C$  atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the  $X$  AO to form a MO permits each participating orbital to decrease in radius and energy. For example, to meet the equipotential condition of the union of the  $(O)C-Cl$   $H_2$ -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor  $C_2$  of Eq. (15.52) for the  $(O)C-Cl$ -bond MO given by Eq. (15.111) is  $C_2(C2sp^3HO \text{ to } Cl) = 0.81317$ . The solution is equivalent to that of the alkyl chloride bond except that the energy parameters corresponding to oscillation in the transition state are matched to those of a carboxylic acid chloride.

As in the case with the  $C-Cl$  group of alkyl chlorides,  $E_r(atom-atom,msp^3.AO)$  of the  $(O)C-Cl$ -bond MO in Eq. (15.52) of alky carboxylic acid chlorides due to the charge donation from the  $C$  and  $Cl$  atoms to the MO is  $-1.44915 eV$  where both energy contributions

are given by Eq. (14.511). This matches the energy of the  $C - C(O)$  functional group with that of the  $(O)C - Cl$  group within the carboxylic acid chloride molecule.

The symbols of the functional groups of alkyl carboxylic acid chlorides are given in Table 15.129. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)),  
5 and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acid chlorides are given in Tables 15.130, 15.131, and 15.132, respectively. The total energy of each alkyl carboxylic acid chloride given in Table 15.133 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.132 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl carboxylic acid chlorides determined using Eqs.  
10 (15.79-15.108) are given in Table 15.134.



Table 15.129. The symbols of functional groups of alkyl carboxylic acid chlorides.

| Functional Group                     | Group Symbol           |
|--------------------------------------|------------------------|
| C-C(O)                               | C=O                    |
| C=O (alkyl carboxylic acid chloride) | C-Cl                   |
| O(C-Cl)                              | C-H (CH <sub>3</sub> ) |
| CH <sub>3</sub> group                | C-H (CH <sub>2</sub> ) |
| CH <sub>2</sub> group                | C-H                    |
| CH (alkyl) group                     | C-C (a)                |
| CC bond (n-C)                        | C-C (b)                |
| CC bond (iso-C)                      | C-C (c)                |
| CC bond (tert-C)                     | C-C (d)                |
| CC (iso to iso-C)                    | C-C (e)                |
| CC (t to t-C)                        | C-C (f)                |
| CC (t to iso-C)                      |                        |

Table 15.130. The geometrical bond parameters of alkyl carboxylic acid chlorides and experimental values [1].

| Parameter            | C-C(O)<br>Group                       | C=O<br>Group                                   | C-Cl<br>Group           | C-H (CH <sub>3</sub> )<br>Group           | C-H (CH <sub>2</sub> )<br>Group           | C-H<br>Group      | C-C (a)<br>Group                  | C-C (b)<br>Group                  | C-C (c)<br>Group                  | C-C (d)<br>Group                  | C-C (e)<br>Group                  | C-C (f)<br>Group                  |
|----------------------|---------------------------------------|------------------------------------------------|-------------------------|-------------------------------------------|-------------------------------------------|-------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| $\alpha$ (°)         | 2.04740                               | 1.29007                                        | 2.32621                 | 1.64920                                   | 1.67122                                   | 1.67465           | 2.12499                           | 2.12499                           | 2.10725                           | 2.12499                           | 2.10725                           | 2.10725                           |
| $\alpha'$ (°)        | 1.43087                               | 1.13977                                        | 1.69136                 | 1.04856                                   | 1.05553                                   | 1.05861           | 1.45744                           | 1.45744                           | 1.45164                           | 1.45744                           | 1.45164                           | 1.45164                           |
| Bond Length          |                                       |                                                |                         |                                           |                                           |                   |                                   |                                   |                                   |                                   |                                   |                                   |
| 2c' (Å)              | 1.51437                               | 1.20628                                        | 1.79005                 | 1.10974                                   | 1.11713                                   | 1.11827           | 1.54280                           | 1.54280                           | 1.53635                           | 1.54280                           | 1.53635                           | 1.53635                           |
| Exp. Bond Length (Å) | 1.520 (acetone)<br>1.518 (2-butanone) | 1.187 (acetyl chloride)<br>1.214 (acetic acid) | 1.798 (acetyl chloride) | 1.107 (C-H propane)<br>1.117 (C-H butane) | 1.107 (C-H propane)<br>1.117 (C-H butane) | 1.122 (isobutane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) |
| $\mu$ (°)            | 1.46439                               | 0.62331                                        | 1.59705                 | 1.27295                                   | 1.29569                                   | 1.29924           | 1.54616                           | 1.54616                           | 1.52750                           | 1.54616                           | 1.52750                           | 1.52750                           |
| $\sigma$             | 0.69887                               | 0.87757                                        | 0.72709                 | 0.63580                                   | 0.63159                                   | 0.63095           | 0.68600                           | 0.68600                           | 0.68888                           | 0.68600                           | 0.68888                           | 0.68888                           |

Table 15.131. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acid chlorides.  $R, R', R''$  are H or alkyl groups.  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{msp}^2, \text{AO})$ .

| Bond                                                         | Atom | $E_r$<br>(eV)<br>Bond 1 | $E_r$<br>(eV)<br>Bond 2 | $E_r$<br>(eV)<br>Bond 3 | $E_r$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>$C2_{sp^2}$<br>(eV) | $r_{\text{final}}$<br>( $a_0$ ) | $E_{\text{calculated}}$<br>(eV)<br>Final | $E(C2_{sp^2})$<br>(eV)<br>Final | $\theta^*$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | $d_1$<br>( $a_0$ ) | $d_2$<br>( $a_0$ ) |
|--------------------------------------------------------------|------|-------------------------|-------------------------|-------------------------|-------------------------|----------------------------------------------|---------------------------------|------------------------------------------|---------------------------------|----------------------------|----------------------------|----------------------------|--------------------|--------------------|
| $H_1C_1C_2(O)-Cl$                                            | Cl   | -0.72457                | 0                       | 0                       | 0                       | -154.41430                                   | 0.87495                         | -15.55033                                | -17.43350                       | 69.62                      | 110.38                     | 30.90                      | 1.99599            | 0.30463            |
| $H_1C_1C_2(O)-Cl$                                            | C    | -1.34946                | -0.72457                | -0.72457                | 0                       | -154.41430                                   | 0.91771                         | -17.62436                                | -17.43350                       | 54.69                      | 125.31                     | 23.23                      | 2.13760            | 0.44625            |
| $H_1C_1C_2(O)-O$                                             | O    | -1.34946                | 0                       | 0                       | 0                       | -154.41430                                   | 1.00000                         | -16.17521                                | -17.43350                       | 137.27                     | 42.73                      | 66.31                      | 0.52193            | 0.61784            |
| $H_1C_1C_2(O)-O$                                             | C    | -1.34946                | -0.72457                | -0.72457                | 0                       | -154.41430                                   | 0.91771                         | -17.62436                                | -17.43350                       | 134.28                     | 45.72                      | 62.45                      | 0.60076            | 0.53901            |
| $H_1C_1C_2(O)-Cl$                                            | C    | -0.72457                | -1.34946                | -0.72457                | 0                       | -154.41430                                   | 0.91771                         | -17.62436                                | -17.43350                       | 59.30                      | 120.70                     | 26.96                      | 1.82495            | 0.39408            |
| $H_1C_1C_2(O)-Cl$                                            | C    | -0.72457                | 0                       | 0                       | 0                       | -152.34026                                   | 0.91771                         | -15.55033                                | -15.55033                       | 73.62                      | 106.38                     | 34.98                      | 1.67762            | 0.24675            |
| $C-H(CH_3)$                                                  | C    | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                   | 0.91771                         | -15.54993                                | -15.54993                       | 77.49                      | 102.51                     | 41.48                      | 1.23564            | 0.18708            |
| $C-H(CH_3)$                                                  | C    | -0.92918                | -0.92918                | 0                       | 0                       | -153.47006                                   | 0.91771                         | -16.68412                                | -16.49325                       | 68.47                      | 111.53                     | 35.84                      | 1.35486            | 0.29933            |
| $C-H(CH_3)$ (ii)                                             | C    | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                   | 0.91771                         | -17.61330                                | -17.42244                       | 61.10                      | 118.90                     | 31.37                      | 1.42988            | 0.37326            |
| $H_1C_1C_2H_2CH_2-$<br>(C-C (a))                             | C    | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                   | 0.91771                         | -15.54993                                | -15.54993                       | 63.82                      | 116.18                     | 30.08                      | 1.83879            | 0.38106            |
| $H_1C_1C_2H_2CH_2-$<br>(C-C (a))                             | C    | -0.92918                | -0.92918                | 0                       | 0                       | -153.47006                                   | 0.91771                         | -16.68412                                | -16.49325                       | 56.41                      | 123.59                     | 26.06                      | 1.90890            | 0.45117            |
| $R-H_1C_1C_2(H_1C_1'-R')HCH_2-$<br>(C-C (b))                 | C    | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                   | 0.91771                         | -17.61330                                | -17.42244                       | 48.30                      | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| $R-H_1C_1C_2(R''-H_2C_2')C_3(R''-H_2C_2')CH_2-$<br>(C-C (c)) | C    | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -154.71860                                   | 0.91771                         | -17.92866                                | -17.73779                       | 48.21                      | 131.79                     | 21.74                      | 1.95734            | 0.50570            |
| $isoC_1C_2(H_1C_1'-R')HCH_2-$<br>(C-C (d))                   | C    | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                   | 0.91771                         | -17.61330                                | -17.42244                       | 48.30                      | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| $isoC_1C_2(R''-H_2C_2')C_3(R''-H_2C_2')CH_2-$<br>(C-C (e))   | C    | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.51399                                   | 0.91771                         | -17.92866                                | -17.73779                       | 50.04                      | 129.96                     | 22.66                      | 1.94462            | 0.49298            |
| $isoC_1C_2(H_1C_1'-R')HCH_2-$<br>(C-C (f))                   | C    | -0.72457                | -0.92918                | -0.92918                | 0                       | -154.19663                                   | 0.91771                         | -17.40869                                | -17.21783                       | 52.78                      | 127.22                     | 24.04                      | 1.97443            | 0.47279            |
| $isoC_1C_2(R''-H_2C_2')C_3(R''-H_2C_2')CH_2-$<br>(C-C (f))   | C    | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.51399                                   | 0.91771                         | -17.92866                                | -17.73779                       | 50.04                      | 129.96                     | 22.66                      | 1.94462            | 0.49298            |

Table 15.132. The energy parameters (eV) of functional groups of alkyl carboxylic acid chlorides.

| Parameters                  | C-Cl(O)<br>Group | C=O<br>Group | C-Cl<br>Group | CH <sub>3</sub><br>Group | CH <sub>2</sub><br>Group | C-H (ii)<br>Group | C-C (a)<br>Group | C-C (b)<br>Group | C-C (c)<br>Group | C-C (d)<br>Group | C-C (e)<br>Group | C-C (f)<br>Group |
|-----------------------------|------------------|--------------|---------------|--------------------------|--------------------------|-------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| $\eta_1$                    | 1                | 2            | 1             | 3                        | 2                        | 1                 | 1                | 1                | 1                | 1                | 1                | 1                |
| $\eta_2$                    | 0                | 0            | 0             | 2                        | 1                        | 0                 | 0                | 0                | 0                | 0                | 0                | 0                |
| $\eta_3$                    | 0                | 0            | 0             | 0                        | 0                        | 0                 | 0                | 0                | 0                | 0                | 0                | 0                |
| $C_1$                       | 0.5              | 0.5          | 0.5           | 0.75                     | 0.75                     | 0.75              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              |
| $C_2$                       | 1                | 1            | 0.81317       | 1                        | 1                        | 1                 | 1                | 1                | 1                | 1                | 1                | 1                |
| $C_3$                       | 1                | 1            | 1             | 1                        | 1                        | 1                 | 1                | 1                | 1                | 1                | 1                | 1                |
| $C_4$                       | 0.91771          | 0.85395      | 1             | 0.91771                  | 0.91771                  | 0.91771           | 0.91771          | 0.91771          | 0.91771          | 0.91771          | 0.91771          | 0.91771          |
| $C_5$                       | 0                | 2            | 1             | 0                        | 1                        | 1                 | 0                | 0                | 0                | 1                | 1                | 0                |
| $C_6$                       | 2                | 4            | 2             | 1                        | 1                        | 1                 | 2                | 2                | 2                | 2                | 2                | 2                |
| $C_7$                       | 0                | 0            | 0             | 3                        | 2                        | 1                 | 0                | 0                | 0                | 0                | 0                | 0                |
| $C_8$                       | 1                | 0.5          | 0.5           | 0.75                     | 0.75                     | 0.75              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              |
| $C_9$                       | 1                | 1            | 0.81317       | 1                        | 1                        | 1                 | 1                | 1                | 1                | 1                | 1                | 1                |
| $C_{10}$                    | 1                | 1            | 1             | 1                        | 1                        | 1                 | 1                | 1                | 1                | 1                | 1                | 1                |
| $V_r$ (eV)                  | -30.19634        | -111.25473   | -29.68411     | -107.32728               | -70.41425                | -35.12015         | -28.79214        | -28.79214        | -29.10112        | -28.79214        | -29.10112        | -29.10112        |
| $V_n$ (eV)                  | 9.50874          | 23.87467     | 8.04432       | 38.92728                 | 25.78002                 | 12.87680          | 9.33352          | 9.33352          | 9.37273          | 9.33352          | 9.37273          | 9.37273          |
| $T$ (eV)                    | 7.37432          | 42.82081     | 6.38036       | 32.53914                 | 21.06675                 | 10.48582          | 6.77464          | 6.77464          | 6.90500          | 6.77464          | 6.90500          | 6.90500          |
| $V_n$ (eV)                  | -3.68716         | -21.41040    | -3.19018      | -16.26957                | -10.53337                | -5.24291          | -3.38732         | -3.38732         | -3.45250         | -3.38732         | -3.45250         | -3.45250         |
| $E_{(a)}(m)$ (eV)           | -14.63489        | 0            | -14.63489     | -15.56407                | -15.56407                | -14.63489         | -15.56407        | -15.56407        | -15.56407        | -15.56407        | -15.56407        | -15.56407        |
| $\Delta E_{(a)}(m)$ (eV)    | 0                | -2.69893     | -1.44915      | 0                        | 0                        | 0                 | 0                | 0                | 0                | 0                | 0                | 0                |
| $E_{(a)}(m)$ (eV)           | -14.63489        | 2.69893      | -13.18574     | -15.56407                | -15.56407                | -14.63489         | -15.56407        | -15.56407        | -15.56407        | -15.56407        | -15.56407        | -15.56407        |
| $E_{(a)}(m)$ (eV)           | -31.63534        | -63.27074    | -31.63536     | -67.69451                | -49.66493                | -31.63533         | -31.63537        | -31.63537        | -31.63535        | -31.63537        | -31.63535        | -31.63535        |
| $E_{(a)}(m)$ (eV)           | -1.44915         | -2.69893     | -1.44915      | 0                        | 0                        | 0                 | -1.85836         | -1.85836         | -1.44915         | -1.85836         | -1.44915         | -1.44915         |
| $E_{(a)}(m)$ (eV)           | -33.08452        | -65.96966    | -33.08452     | -67.69450                | -49.66493                | -31.63537         | -33.49373        | -33.49373        | -33.08452        | -33.49373        | -33.08452        | -33.08452        |
| $\omega$ ( $10^{15}$ rad/s) | 16.4962          | 59.4034      | 7.42995       | 24.9286                  | 24.2751                  | 24.1759           | 9.43699          | 9.43699          | 15.4846          | 9.43699          | 9.55643          | 9.55643          |
| $I_{(a)}(eV)$               | 10.85807         | 39.10034     | 4.89052       | 16.40846                 | 15.97831                 | 15.91299          | 6.21159          | 6.21159          | 10.19220         | 6.21159          | 6.29021          | 6.29021          |
| $I_{(a)}(eV)$               | -0.21568         | -0.40804     | -0.14475      | -0.25352                 | -0.25017                 | -0.24966          | -0.16515         | -0.16515         | -0.20896         | -0.16515         | -0.16416         | -0.16416         |
| $E_{(a)}(eV)$               | 0.14655          | 0.21077      | 0.09063       | 0.35532                  | 0.35532                  | 0.35532           | 0.12312          | 0.17978          | 0.09944          | 0.12312          | 0.12312          | 0.12312          |
| $E_{(a)}(eV)$               | [28]             | [12]         | [34]          | (Eq. (13.458))           | (Eq. (13.458))           | (Eq. (13.458))    | [2]              | [4]              | [5]              | [2]              | [2]              | [2]              |
| $E_{(a)}(eV)$               | -0.14240         | -0.30266     | -0.09943      | -0.22757                 | -0.14502                 | -0.07200          | -0.10359         | -0.07526         | -0.15924         | -0.10359         | -0.10260         | -0.10260         |
| $E_{(a)}(eV)$               | 0.14803          | 0.11441      | 0.14803       | 0.14803                  | 0.14803                  | 0.14803           | 0.14803          | 0.14803          | 0.14803          | 0.14803          | 0.14803          | 0.14803          |
| $I_{(a)}(eV)$               | -33.22692        | -66.57498    | -33.18395     | -67.92207                | -49.80996                | -31.70737         | -33.59732        | -33.49373        | -33.24376        | -33.59732        | -33.18712        | -33.18712        |
| $I_{(a)}(eV)$               | -14.63489        | -14.63489    | -14.63489     | -14.63489                | -14.63489                | -14.63489         | -14.63489        | -14.63489        | -14.63489        | -14.63489        | -14.63489        | -14.63489        |
| $I_{(a)}(eV)$               | 0                | 0            | 0             | -13.59844                | -13.59844                | -13.59844         | 0                | 0                | 0                | 0                | 0                | 0                |
| $I_{(a)}(eV)$               | 3.95714          | 7.80660      | 3.76614       | 12.49186                 | 7.83016                  | 3.32601           | 4.32754          | 4.29921          | 3.97398          | 4.17951          | 3.62128          | 3.91734          |

Table 15.133. The total bond energies of alkyl carboxylic acid chlorides calculated using the functional group composition and the energies of Table 15.102 compared to the experimental values [3].

| Formula                           | C-Cl(O)<br>Group | C=O<br>Group | C-Cl<br>Group | CH <sub>3</sub><br>Group | CH <sub>2</sub><br>Group | CH<br>Group | C-C (a)<br>Group | C-C (b)<br>Group | C-C (c)<br>Group | C-C (d)<br>Group | C-C (e)<br>Group | C-C (f)<br>Group | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|-----------------------------------|------------------|--------------|---------------|--------------------------|--------------------------|-------------|------------------|------------------|------------------|------------------|------------------|------------------|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>2</sub> H <sub>3</sub> ClO | 1                | 1            | 1             | 1                        | 0                        | 0           | 0                | 0                | 0                | 0                | 0                | 0                | 28.03174                                | 27.990                                    | -0.00115       |

Table 15.134. The bond angle parameters of alkyl carboxylic acid chlorides and experimental values [1]. In the calculation of  $\theta_i$ , the parameters from the preceding angle were used.  $E_T = E_T(\text{atom} - \text{atom.msp}^2 \cdot \text{AO})$ .

| Atoms of Angle               | $2c_1$<br>Bond 1<br>( $a_0$ ) | $2c_2$<br>Bond 2<br>( $a_0$ ) | $2c_3$<br>Terminal<br>Atoms ( $a_0$ ) | $E_{\text{calc}}^{\text{calc}}$<br>Atom 1 | Atom 1<br>Hybridization<br>Designation<br>(Table 15.3.A) | $E_{\text{calc}}^{\text{calc}}$<br>Atom 2 | Atom 2<br>Hybridization<br>Designation<br>(Table 15.3.A) | $c_1$<br>Atom 1 | $c_2$<br>Atom 2         | $C_1$ | $C_2$                   | $c_3$ | $E_T$<br>(eV) | $\theta_r$<br>( $^\circ$ ) | $\theta_l$<br>( $^\circ$ ) | $\theta_s$<br>( $^\circ$ ) | Cal. $\theta$<br>( $^\circ$ ) | Exp. $\theta$<br>( $^\circ$ ) |
|------------------------------|-------------------------------|-------------------------------|---------------------------------------|-------------------------------------------|----------------------------------------------------------|-------------------------------------------|----------------------------------------------------------|-----------------|-------------------------|-------|-------------------------|-------|---------------|----------------------------|----------------------------|----------------------------|-------------------------------|-------------------------------|
| $\angle C_1 C_2 O$           | 2.86175                       | 2.27954                       | 4.5926                                | -16.68411                                 | 24                                                       | -13.61806                                 | O                                                        | 0.81549         | 0.83395<br>(Eq. 15.113) | 1     | 1                       | 1     | -1.6376       |                            |                            |                            | 125.70                        |                               |
| $\angle C_1 C_2 C_3$         | 2.86175                       | 3.38271                       | 5.1539                                | -15.75493                                 | 7                                                        | -12.96764<br>( $C_1$ )                    | Cl                                                       | 0.86359         | 0.86359                 | 1     | 0.81317<br>(Eq. 15.111) | 1     | -0.92918      |                            |                            |                            | 110.98                        | 111.6<br>(acetyl<br>chloride) |
| $\angle O C_2 C_1$           | 2.27954                       | 3.38271                       | 4.9841                                | -16.68412<br>( $O$ )                      | 25                                                       | -15.55033<br>( $C_1$ )                    | 5                                                        | 0.81549         | 0.87495                 | 1     | 0.81317<br>(Eq. 15.111) | 1     | -0.92918      |                            |                            |                            | 122.13                        | 121.2<br>(acetyl<br>chloride) |
| Methyl<br>$\angle H C_2 C_1$ | 2.11106                       | 2.11106                       | 3.4252                                | -15.75493                                 | 7                                                        | H                                         | H                                                        | 0.86359         | 1                       | 1     | 1                       | 0.75  | 0             |                            |                            |                            | 108.44                        | 107<br>(propane)              |
| $\angle C_1 C_2 C_3$         |                               |                               |                                       |                                           |                                                          |                                           |                                                          |                 |                         |       |                         |       |               | 69.51                      |                            |                            | 110.49                        | 113.8<br>(isobutane)          |
| $\angle C_1 C_2 H$           |                               |                               |                                       |                                           |                                                          |                                           |                                                          |                 |                         |       |                         |       |               | 69.51                      |                            |                            | 110.49                        | 111.4<br>(isobutane)          |
| Methyl<br>$\angle H C_2 C_3$ | 2.09711                       | 2.09711                       | 3.4252                                | -15.75493                                 | 7                                                        | H                                         | H                                                        | 0.86359         | 1                       | 1     | 1                       | 0.75  | 0             |                            |                            |                            | 109.50                        | 108.6<br>(acetyl<br>chloride) |
| $\angle C_1 C_2 C_3$         |                               |                               |                                       |                                           |                                                          |                                           |                                                          |                 |                         |       |                         |       |               |                            |                            |                            | 109.44                        | 108.5<br>(acetone)            |
| $\angle C_1 C_2 H$           |                               |                               |                                       |                                           |                                                          |                                           |                                                          |                 |                         |       |                         |       |               | 70.56                      |                            |                            | 109.44                        |                               |
| $\angle C_1 C_2 C_3$         | 2.91547                       | 2.91547                       | 4.7958                                | -16.68412                                 | 25                                                       | -16.68412<br>( $C_3$ )                    | 25                                                       | 0.81549         | 0.81549                 | 1     | 1                       | 1     | -1.85336      |                            |                            |                            | 110.67                        | 110.8<br>(isobutane)          |
| $\angle C_1 C_2 H$           | 2.91547                       | 2.11323                       | 4.1633                                | -15.55033<br>( $C_3$ )                    | 5                                                        | -14.82575<br>( $C_3$ )                    | 1                                                        | 0.87495         | 0.91771                 | 0.75  | 1                       | 0.75  | 0             |                            |                            |                            | 110.76                        |                               |
| $\angle C_1 C_2 H$           | 2.91547                       | 2.09711                       | 4.1633                                | -15.55033<br>( $C_3$ )                    | 5                                                        | -14.82575<br>( $C_3$ )                    | 1                                                        | 0.87495         | 0.91771                 | 0.75  | 1                       | 0.75  | 0             |                            |                            |                            | 111.27                        | 111.4<br>(isobutane)          |
| $\angle C_1 C_2 C_3$         | 2.90327                       | 2.90327                       | 4.7958                                | -15.55033<br>( $C_3$ )                    | 5                                                        | -14.82575<br>( $C_3$ )                    | 1                                                        | 0.87495         | 0.91771                 | 0.75  | 1                       | 0.75  | -1.85336      |                            |                            |                            | 111.27                        | 111.4<br>(isobutane)          |
| $\angle C_1 C_2 C_3$         |                               |                               |                                       |                                           |                                                          |                                           |                                                          |                 |                         |       |                         |       |               | 72.50                      |                            |                            | 107.50                        |                               |

# CARBOXYLIC ACID ANHYDRIDES ( $C_nH_{2n-2}O_3$ , $n = 2, 3, 4, 5, \dots, \infty$ )

The alkyl carboxylic acid anhydrides,  $C_nH_{2n-2}O_3$ , have two  $(O)C-O$  moieties that each comprise  $C=O$  and  $C-O$  functional groups. The single bond of carbon to the carbonyl carbon atom,  $C-C(O)$ , is also a functional group. The alkyl portion of the alkyl carboxylic acid anhydride may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The  $n$ -alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and  $t$ -butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to  $t$ -butyl, and  $t$ -butyl to  $t$ -butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acid anhydrides are equivalent to those in branched-chain alkanes.

The alkyl carboxylic acid anhydride  $C=O$  and  $C-C(O)$  groups are equivalent to those given in the Carboxylic Acid Esters section and the Ketones section, respectively. The values of  $E_r(atom-atom, msp^3.AO)$  given in these sections are  $-2.69893 eV$  and  $-1.44915 eV$ , respectively. The  $C-O$  group is also equivalent to that given in the Carboxylic Acid Esters section except that  $E_r(atom-atom, msp^3.AO)$  is equivalent to that of an alkyl ether as given in the corresponding section and the energy terms due to oscillation in the transition state are matched to that of a carboxylic acid anhydride.

For the  $C-O$  group,  $E_r(atom-atom, msp^3.AO)$  is  $-1.65376 eV$ . It is based on the energy match between the  $O$  AO and the  $C2sp^3$  HO of each  $C-C(O)$  group and is given by the linear combination of  $-0.72457 eV$  (Eq. (14.151)) and  $-0.92918 eV$  (Eq. (14.513)), respectively. This matches  $-0.72457 eV$ , the energy contribution of each of the  $C2sp^3$  HOs to each  $C-C(O)$  functional group, with that of the corresponding energy component of the  $C-O$  group and gives a minimum energy within the carboxylic acid anhydride molecule.

The symbols of the functional groups of alkyl carboxylic acid anhydrides are given in Table 15.135. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acid anhydrides are given in Tables 15.136, 15.137, and 15.138, respectively. The total energy of each alkyl

carboxylic acid anhydride given in Table 15.139 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.138 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl carboxylic acid anhydrides determined using Eqs. (15.79-15.108) are given in Table 15.140.

Table 1.5.135. The symbols of functional groups of alkyl carboxylic acid anhydrides.

| Functional Group      | Group Symbol           |
|-----------------------|------------------------|
| C-C(O)                | C-C(O)                 |
| C=O                   | C=O                    |
| (O)C-O                | C-O                    |
| CH <sub>3</sub> group | C-H (CH <sub>3</sub> ) |
| CH <sub>2</sub> group | C-H (CH <sub>2</sub> ) |
| CH (alkyl) group      | C-H                    |
| CC bond (n-C)         | C'-C' (a)              |
| CC bond (iso-C)       | C'-C' (b)              |
| CC bond (tert-C)      | C'-C' (c)              |
| CC (iso to iso-C)     | C'-C' (d)              |
| CC (t to t-C)         | C'-C' (e)              |
| CC (t to iso-C)       | C'-C' (f)              |

Table 1.5.136. The geometrical bond parameters of alkyl carboxylic acid anhydrides and experimental values [1].

| Parameter                | C-C(O)<br>Group                       | C=O<br>Group        | C-O<br>Group                | C-H (CH <sub>3</sub> )<br>Group           | C'-H (CH <sub>3</sub> )<br>Group          | C'-C' (a)<br>Group                   | C'-C' (b)<br>Group                   | C'-C' (c)<br>Group                   | C'-C' (d)<br>Group                   | C'-C' (e)<br>Group                   | C'-C' (f)<br>Group                   |
|--------------------------|---------------------------------------|---------------------|-----------------------------|-------------------------------------------|-------------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| $a$ (Å)                  | 2.04740                               | 1.25907             | 1.73490                     | 1.64920                                   | 1.67122                                   | 2.12499                              | 2.12499                              | 2.10725                              | 2.12499                              | 2.10725                              | 2.10725                              |
| $c'$ (Å)                 | 1.45087                               | 1.13977             | 1.31716                     | 1.04856                                   | 1.05553                                   | 1.45744                              | 1.45744                              | 1.45164                              | 1.45744                              | 1.45164                              | 1.45164                              |
| Bond Length<br>$2c'$ (Å) | 1.51437                               | 1.20638             | 1.39402                     | 1.10974                                   | 1.11713                                   | 1.54280                              | 1.54280                              | 1.53635                              | 1.54280                              | 1.53635                              | 1.53635                              |
| Exp. Bond Length<br>(Å)  | 1.520 (acetone)<br>1.518 (2-butanone) | 1.214 (acetic acid) | 1.393 (avg. methyl formate) | 1.107 (C-H propane)<br>1.117 (C-H butane) | 1.107 (C-H propane)<br>1.117 (C-H butane) | 1.532 (propane)<br>1.531 (isobutane) | 1.532 (propane)<br>1.531 (isobutane) | 1.532 (propane)<br>1.531 (isobutane) | 1.532 (propane)<br>1.531 (isobutane) | 1.532 (propane)<br>1.531 (isobutane) | 1.532 (propane)<br>1.531 (isobutane) |
| $b_1, c'$ (Å)            | 1.46459                               | 0.62331             | 1.12915                     | 1.27295                                   | 1.29569                                   | 1.54616                              | 1.54616                              | 1.52750                              | 1.54616                              | 1.52750                              | 1.52750                              |
| $e$                      | 0.69887                               | 0.87737             | 0.75921                     | 0.63380                                   | 0.63159                                   | 0.68600                              | 0.68600                              | 0.68888                              | 0.68600                              | 0.68888                              | 0.68888                              |

Table 15.137. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acid anhydrides.  $R, R', R''$  are H or alkyl groups.  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{map}^3, \text{AO})$ .

| Bond                                       | Atom  | $E_r$<br>(eV)<br>Bond 1 | $E_r$<br>(eV)<br>Bond 2 | $E_r$<br>(eV)<br>Bond 3 | $E_r$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>C2sp <sup>3</sup><br>(eV) | $r_{\text{final}}$<br>(a <sub>0</sub> ) | $r_{\text{initial}}$<br>(a <sub>0</sub> ) | $E_{\text{electron}}$<br>(eV)<br>Final | $E(\text{C2sp}^3)$<br>(eV)<br>Final | $\theta'$<br>(°) | $\theta_1$<br>(°) | $\theta_2$<br>(°) | $d_1$<br>(a <sub>0</sub> ) | $d_2$<br>(a <sub>0</sub> ) |
|--------------------------------------------|-------|-------------------------|-------------------------|-------------------------|-------------------------|----------------------------------------------------|-----------------------------------------|-------------------------------------------|----------------------------------------|-------------------------------------|------------------|-------------------|-------------------|----------------------------|----------------------------|
| $RC_1H_2C_2(O) - O_n - C_n(O)C_1H_2R'$     | $O_n$ | -0.82688                | -0.82688                | 0                       | 0                       | -154.51660                                         | 0.82562                                 | 1.00000                                   | -16.47951                              | -17.53580                           | 98.32            | 81.68             | 46.34             | 1.19766                    | 0.11949                    |
| $RC_1H_2C_2(O) - O_n - C_n(O)C_1H_2R'$     | $C_n$ | -0.82688                | -1.34946                | -0.82688                | 0                       | -154.51660                                         | 0.76753                                 | 0.91771                                   | -17.72667                              | -17.53580                           | 93.21            | 86.79             | 42.74             | 1.27417                    | 0.04298                    |
| $RC_1H_2[R(C_1H_2C_2(O)_n)C_n]C_n = O_n$   | $O_n$ | -1.34946                | 0                       | 0                       | 0                       | -154.51660                                         | 0.84115                                 | 1.00000                                   | -16.17521                              | -17.53580                           | 137.27           | 42.73             | 66.31             | 0.32193                    | 0.61794                    |
| $RC_1H_2[R(C_1H_2C_2(O)_n)C_n]C_n = O_n$   | $C_n$ | -1.34946                | -0.72457                | -0.82688                | 0                       | -154.51660                                         | 0.76753                                 | 0.91771                                   | -17.72667                              | -17.53580                           | 134.08           | 45.92             | 62.20             | 0.60283                    | 0.33394                    |
| $RH_2C_n - C_n(O)OC_n(O)C_1H_2R'$          | $C_n$ | -0.72457                | -1.34946                | -0.82688                | 0                       | -154.51660                                         | 0.76753                                 | 0.91771                                   | -17.72667                              | -17.53580                           | 58.35            | 121.45            | 26.56             | 1.83135                    | 0.40045                    |
| $H_1C_n - C_n(O)OC_n(O)C_1H_2R'$           | $C_n$ | -0.72457                | 0                       | 0                       | 0                       | -152.34026                                         | 0.87495                                 | 0.91771                                   | -15.55033                              | -15.55946                           | 73.62            | 106.58            | 34.98             | 1.67762                    | 0.24675                    |
| $RH_2C_n - C_n(O)OC_n(O)C_1H_2R'$          | $C_n$ | -0.72457                | -0.92918                | 0                       | 0                       | -153.20945                                         | 0.82362                                 | 0.91771                                   | -16.47951                              | -16.28865                           | 67.40            | 112.60            | 31.56             | 1.74821                    | 0.31734                    |
| $C' - H \{CH_3\}$                          | $C'$  | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                         | 0.86359                                 | 0.91771                                   | -15.75493                              | -15.54407                           | 77.49            | 102.51            | 41.48             | 1.23564                    | 0.18708                    |
| $C' - H \{CH_3\}$                          | $C'$  | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                         | 0.81549                                 | 0.91771                                   | -16.68412                              | -16.49325                           | 68.47            | 111.53            | 35.84             | 1.35486                    | 0.29933                    |
| $C' - H \{CH_3\}$ (ii)                     | $C'$  | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                         | 0.77247                                 | 0.91771                                   | -17.61330                              | -17.42244                           | 61.10            | 118.90            | 31.37             | 1.42988                    | 0.37326                    |
| $H_1C_nC_nH_2C_nH_2 -$<br>(C'-C' (aa))     | $C_n$ | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                         | 0.86359                                 | 0.91771                                   | -15.75493                              | -15.54407                           | 63.82            | 116.18            | 30.08             | 1.83879                    | 0.38106                    |
| $H_1C_nC_nH_2C_nH_2 -$<br>(C'-C' (aa))     | $C_n$ | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                         | 0.81549                                 | 0.91771                                   | -16.68412                              | -16.49325                           | 56.41            | 123.59            | 26.06             | 1.90890                    | 0.45117                    |
| $R - H_2C_nC_nH_2C_nH_2 -$<br>(C'-C' (bb)) | $C_n$ | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                         | 0.77247                                 | 0.91771                                   | -17.61330                              | -17.42244                           | 48.30            | 131.70            | 21.90             | 1.97162                    | 0.51388                    |
| $R - H_2C_nC_nH_2C_nH_2 -$<br>(C'-C' (bb)) | $C_n$ | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -154.71860                                         | 0.75889                                 | 0.91771                                   | -17.92866                              | -17.73779                           | 48.21            | 131.79            | 21.74             | 1.95734                    | 0.50570                    |
| $isoC_nC_nH_2C_nH_2 -$<br>(C'-C' (cc))     | $C_n$ | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                         | 0.77247                                 | 0.91771                                   | -17.61330                              | -17.42244                           | 48.30            | 131.70            | 21.90             | 1.97162                    | 0.51388                    |
| $isoC_nC_nH_2C_nH_2 -$<br>(C'-C' (cc))     | $C_n$ | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -154.51399                                         | 0.76765                                 | 0.91771                                   | -17.92866                              | -17.73779                           | 50.04            | 129.96            | 22.66             | 1.94462                    | 0.49298                    |
| $isoC_nC_nH_2C_nH_2 -$<br>(C'-C' (cc))     | $C_n$ | -0.72457                | -0.72457                | -0.92918                | 0                       | -154.19605                                         | 0.78155                                 | 0.91771                                   | -17.40869                              | -17.21763                           | 52.78            | 127.22            | 24.04             | 1.92443                    | 0.47279                    |
| $isoC_nC_nH_2C_nH_2 -$<br>(C'-C' (ff))     | $C_n$ | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.51399                                         | 0.76765                                 | 0.91771                                   | -17.92866                              | -17.73779                           | 50.04            | 129.96            | 22.66             | 1.94462                    | 0.49298                    |



Table 15.138. The energy parameters (eV) of functional groups of alkyl carboxylic acid anhydrides.

| Parameters                       | C-C (O)   | C=O        | C-O       | C-H <sub>3</sub> | C-H <sub>2</sub> | C-H (H)   | C-C (a)   | C-C (b)   | C-C (c)   | C-C (d)   | C-C (e)   | C-C (f)   |
|----------------------------------|-----------|------------|-----------|------------------|------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Group                            | Group     | Group      | Group     | Group            | Group            | Group     | Group     | Group     | Group     | Group     | Group     | Group     |
| $\eta_1$                         | 1         | 2          | 1         | 3                | 2                | 1         | 1         | 1         | 1         | 1         | 1         | 1         |
| $\eta_2$                         | 0         | 0          | 0         | 2                | 1                | 0         | 0         | 0         | 0         | 0         | 0         | 0         |
| $\eta_3$                         | 0         | 0          | 0         | 0                | 0                | 0         | 0         | 0         | 0         | 0         | 0         | 0         |
| $C_1$                            | 0.5       | 0.5        | 0.5       | 0.75             | 0.75             | 0.75      | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       |
| $C_2$                            | 1         | 1          | 1         | 1                | 1                | 1         | 1         | 1         | 1         | 1         | 1         | 1         |
| $C_3$                            | 1         | 1          | 1         | 1                | 1                | 1         | 1         | 1         | 1         | 1         | 1         | 1         |
| $C_4$                            | 0.91771   | 0.85395    | 0.85395   | 0.91771          | 0.91771          | 0.91771   | 0.91771   | 0.91771   | 0.91771   | 0.91771   | 0.91771   | 0.91771   |
| $C_5$                            | 0         | 2          | 0         | 0                | 1                | 1         | 0         | 0         | 0         | 1         | 1         | 0         |
| $C_6$                            | 2         | 4          | 2         | 1                | 1                | 1         | 2         | 2         | 2         | 2         | 2         | 2         |
| $C_7$                            | 0         | 0          | 0         | 3                | 2                | 1         | 0         | 0         | 0         | 0         | 0         | 0         |
| $C_8$                            | 1         | 0.5        | 0.5       | 0.75             | 0.75             | 0.75      | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       |
| $C_9$                            | 1         | 1          | 1         | 1                | 1                | 1         | 1         | 1         | 1         | 1         | 1         | 1         |
| $C_{10}$                         | -30.19634 | -111.25473 | -35.08488 | -107.32728       | -70.41425        | -35.12015 | -28.79214 | -28.79214 | -28.79214 | -28.79214 | -28.79214 | -28.79214 |
| $V_1$ (eV)                       | 9.50874   | 23.87467   | 10.32968  | 38.92728         | 25.78002         | 12.87680  | 9.33352   | 9.33352   | 9.33352   | 9.33352   | 9.33352   | 9.33352   |
| $T$ (eV)                         | 7.37432   | 42.82081   | 10.11150  | 32.53914         | 21.06675         | 10.48582  | 6.77464   | 6.77464   | 6.77464   | 6.77464   | 6.77464   | 6.77464   |
| $V_2$ (eV)                       | -3.68716  | -21.41040  | -5.05575  | -16.26957        | -10.53337        | -5.24291  | -3.38732  | -3.38732  | -3.38732  | -3.38732  | -3.38732  | -3.38732  |
| $E_1$ (eV)                       | -14.63489 | 0          | -14.63489 | -15.56407        | -15.56407        | -14.63489 | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 |
| $\Delta E_{1,10}$ (eV)           | 0         | -2.69893   | -2.69893  | 0                | 0                | 0         | 0         | 0         | 0         | 0         | 0         | 0         |
| $E_2$ (eV)                       | -14.63489 | 2.69893    | -11.93596 | -15.56407        | -15.56407        | -14.63489 | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 |
| $E_3$ (eV)                       | -31.63534 | -63.27074  | -31.63534 | -67.69451        | -49.66493        | -31.63533 | -31.63537 | -31.63537 | -31.63537 | -31.63537 | -31.63537 | -31.63537 |
| $E_4$ (eV)                       | -1.44915  | -2.69893   | -1.63376  | 0                | 0                | 0         | -1.85836  | -1.85836  | -1.85836  | -1.85836  | -1.85836  | -1.85836  |
| $E_5$ (eV)                       | -33.08452 | -65.96966  | -33.28912 | -67.69450        | -49.66493        | -31.63537 | -33.49373 | -33.49373 | -33.49373 | -33.49373 | -33.49373 | -33.49373 |
| $\omega$ (10 <sup>6</sup> rad/s) | 16.4962   | 59.4034    | 24.3637   | 24.9286          | 24.2751          | 24.1759   | 9.43699   | 9.43699   | 9.43699   | 9.43699   | 9.43699   | 9.43699   |
| $E_6$ (eV)                       | 10.85807  | 39.10034   | 16.03660  | 16.40846         | 15.97831         | 15.91299  | 6.21159   | 6.21159   | 6.21159   | 6.21159   | 6.21159   | 6.21159   |
| $E_7$ (eV)                       | -0.21568  | -0.40804   | -0.26373  | -0.25532         | -0.25017         | -0.24966  | -0.16315  | -0.16315  | -0.16315  | -0.16315  | -0.16315  | -0.16315  |
| $E_8$ (eV)                       | 0.14655   | 0.21077    | 0.13638   | 0.35532          | 0.35532          | 0.12312   | 0.12312   | 0.12312   | 0.12312   | 0.12312   | 0.12312   | 0.12312   |
| $E_9$ (eV)                       | 1281      | 1121       | 1351      | 1351             | 1351             | 1351      | 1351      | 1351      | 1351      | 1351      | 1351      | 1351      |
| $E_{10}$ (eV)                    | -0.14240  | -0.30266   | -0.19554  | -0.22737         | -0.14502         | -0.07200  | -0.10359  | -0.07200  | -0.10359  | -0.10359  | -0.10359  | -0.10359  |
| $E_{11}$ (eV)                    | 0.14803   | 0.11441    | 0.14803   | 0.14803          | 0.14803          | 0.14803   | 0.14803   | 0.14803   | 0.14803   | 0.14803   | 0.14803   | 0.14803   |
| $E_{12}$ (eV)                    | -33.22692 | -66.57498  | -33.48466 | -67.92207        | -49.80996        | -31.70737 | -33.59732 | -33.59732 | -33.59732 | -33.59732 | -33.59732 | -33.59732 |
| $E_{13}$ (eV)                    | -14.63489 | -14.63489  | -14.63489 | -14.63489        | -14.63489        | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{14}$ (eV)                    | 0         | 0          | 0         | -15.59844        | -15.59844        | -15.59844 | 0         | 0         | 0         | 0         | 0         | 0         |
| $E_{15}$ (eV)                    | 3.95714   | 7.80660    | 4.21488   | 12.49186         | 7.83016          | 3.52601   | 4.32754   | 4.29921   | 4.29921   | 4.29921   | 4.29921   | 4.29921   |

Table 15.139. The total bond energies of alkyl carboxylic acid anhydrides calculated using the functional group composition and the energies of Table 15.138 compared to the experimental values [3].

| Formula                                      | Name                | C-C (O) | C=O | C-O | C-H <sub>3</sub> | C-H <sub>2</sub> | C-H | C-C (a) | C-C (b) | C-C (c) | C-C (d) | C-C (e) | C-C (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|----------------------------------------------|---------------------|---------|-----|-----|------------------|------------------|-----|---------|---------|---------|---------|---------|---------|-----------------------------------|-------------------------------------|----------------|
| C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> | Acetic anhydride    | 2       | 2   | 2   | 2                | 2                | 0   | 0       | 0       | 0       | 0       | 0       | 0       | 56.94096                          | 56.948                              | 0.00013        |
| C <sub>4</sub> H <sub>6</sub> O <sub>4</sub> | Propanoic anhydride | 2       | 2   | 2   | 2                | 2                | 0   | 0       | 0       | 0       | 0       | 0       | 0       | 81.25636                          | 81.401                              | 0.00177        |



# NITRILES ( $C_nH_{2n-1}N$ , $n = 2, 3, 4, 5 \dots \infty$ )

The nitriles,  $C_nH_{2n-1}N$ , comprise a  $C \equiv N$  functional group, and the single bond of carbon to the nitrile carbon atom,  $C - CN$ , is also a functional group. The alkyl portion of the nitrile may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C - C$  bonds can be identified. The n-alkane  $C - C$  bond is the same as that of straight-chain alkanes. In addition, the  $C - C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C - C$  bonds comprise functional groups. The branched-chain-alkane groups in nitriles are equivalent to those in branched-chain alkanes.

The nitrile  $C \equiv N$  is solved equivalently to acetylene as given in the Acetylene Molecule section except that the energy for  $\Delta E_{H_2MO}(AO/HO)$  is two times that given in Eq. (14.343), 16.20002 eV, in order to match the  $N$  AOs to that of the nitrile  $C2sp^3$  HO having a bond order of three.  $E_T(atom - atom, msp^3.AO)$  of the  $C \equiv N$  functional group is -1.56513 eV (Eq. (14.342)) corresponding to the third-order bonded  $C2sp^3$  HO.

The  $C - CN$  functional group is equivalent to that of an alkyl  $C - C$  group given in the Continuous-Chain Alkanes section except that  $E_T(H_2MO)$  and  $\bar{E}_{Kvib}$  are those corresponding to a nitrile. As given in the Continuous-Chain Alkanes section,  $E_T(atom - atom, msp^3.AO)$  of the alkyl  $C - C$  group is -1.85836 eV where both energy contributions are given by Eq. (14.513). It is based on energy matching within the nitrile. It corresponds to the maximum-magnitude energy contributions of a single-bonded and a third-order bonded  $C2sp^3$  HO.

The symbols of the functional groups of nitriles are given in Table 15.141. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of nitriles are given in Tables 15.142, 15.143, and 15.144, respectively. The total energy of each nitrile given in Table 15.139 was calculated as the sum over the integer multiple of each  $E_D(group)$  of Table 15.144 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the

$E_D(\text{group})$  (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of nitriles determined using Eqs. (15.79-15.108) are given in Table 15.146. The C of the  $C \equiv N$  group can further bond with only one atom, and the bond is linear as a minimum of energy as in the case of acetylene and alkynes.

Table 15.141. The symbols of functional groups of nitriles.

| Functional Group      | Group Symbol           |
|-----------------------|------------------------|
| C-CN                  | C-C (i)                |
| CN                    | C≡N                    |
| CH <sub>3</sub> group | C-H (CH <sub>3</sub> ) |
| CH <sub>2</sub> group | C-H (CH <sub>2</sub> ) |
| CH (alkyl) group      | C-H                    |
| CC bond (n-C)         | C-C (a)                |
| CC bond (iso-C)       | C-C (b)                |
| CC bond (tert-C)      | C-C (c)                |
| CC (iso to iso-C)     | C-C (d)                |
| CC (t to t-C)         | C-C (e)                |
| CC (t to iso-C)       | C-C (f)                |

Table 15.142. The geometrical bond parameters of nitriles and experimental values [1].

| Parameter            | C-C (i)<br>Group     | C≡N<br>Group         | C-H (CH <sub>3</sub> )<br>Group           | C-H (CH <sub>2</sub> )<br>Group           | C-H<br>Group      | C-C (a)<br>Group                  | C-C (b)<br>Group                  | C-C (c)<br>Group                  | C-C (d)<br>Group                  | C-C (e)<br>Group                  | C-C (f)<br>Group                  |
|----------------------|----------------------|----------------------|-------------------------------------------|-------------------------------------------|-------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| $\alpha$ (°)         | 1.91255              | 1.20590              | 1.64920                                   | 1.67122                                   | 1.67465           | 2.12499                           | 2.12499                           | 2.10725                           | 2.12499                           | 2.10725                           | 2.10725                           |
| $\epsilon'$ (°)      | 1.38295              | 1.09813              | 1.04856                                   | 1.05553                                   | 1.05661           | 1.45744                           | 1.45744                           | 1.45164                           | 1.45744                           | 1.45164                           | 1.45164                           |
| Bond Length          | 1.46365              | 1.16221              | 1.10974                                   | 1.11713                                   | 1.11827           | 1.54280                           | 1.54280                           | 1.53635                           | 1.54280                           | 1.53635                           | 1.53635                           |
| Exp. Bond Length (Å) | 1.468 (acetonitrile) | 1.159 (acetonitrile) | 1.107 (C-H propane)<br>1.117 (C-H butane) | 1.107 (C-H propane)<br>1.117 (C-H butane) | 1.122 (isobutane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) |
| $h_{\text{C}}$ (°)   | 1.382110             | 0.49828              | 1.27295                                   | 1.29569                                   | 1.29924           | 1.54616                           | 1.54616                           | 1.52750                           | 1.54616                           | 1.52750                           | 1.52750                           |
| $\epsilon$           | 0.72309              | 0.91064              | 0.63380                                   | 0.63159                                   | 0.63095           | 0.68600                           | 0.68600                           | 0.68888                           | 0.68600                           | 0.68888                           | 0.68888                           |

Table 15.143. The MO to HO intercept geometrical bond parameters of nitriles.  $R, R', R''$  are H or alkyl groups.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{usp}^3, \text{AO})$ .

| Bond                                                       | Atom  | $E_T$<br>(eV)<br>Bond 1 | $E_T$<br>(eV)<br>Bond 2 | $E_T$<br>(eV)<br>Bond 3 | $E_T$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>( $\text{C}2\text{sp}^3$ )<br>(eV) | $r_{\text{final}}$<br>( $a_0$ ) | $r_{\text{bond}}$<br>( $a_0$ ) | $E_{\text{calculated}}$<br>(eV)<br>Final | $E(\text{C}2\text{sp}^3)$<br>(eV)<br>Final | $\theta^*$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | $d_1$<br>( $a_0$ ) | $d_2$<br>( $a_0$ ) |
|------------------------------------------------------------|-------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------------------------------------------|---------------------------------|--------------------------------|------------------------------------------|--------------------------------------------|----------------------------|----------------------------|----------------------------|--------------------|--------------------|
| $RH_2C_2C_2N$                                              | N     | -0.78257                | 0                       | 0                       | 0                       | -153.32744                                                  | 0.93084                         | 0.87170                        | -15.60832                                | -                                          | 147.01                     | 32.99                      | 72.28                      | 0.36099            | 0.73114            |
| $RH_2C_2C_2N$                                              | $C_u$ | -0.78257                | -0.92918                | 0                       | 0                       | -153.32744                                                  | 0.91771                         | 0.82272                        | -16.37350                                | -16.34664                                  | 145.42                     | 34.58                      | 69.58                      | 0.42077            | 0.67736            |
| $RH_2C_2C_2N$                                              | $C_s$ | -0.92918                | -0.78257                | 0                       | 0                       | -153.32744                                                  | 0.91771                         | 0.82272                        | -16.37350                                | -16.34664                                  | 81.32                      | 98.68                      | 38.00                      | 1.50718            | 0.12023            |
| $H_2C_2C_2N$                                               | $C_b$ | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                                  | 0.91771                         | 0.86359                        | -15.75493                                | -15.56407                                  | 83.50                      | 94.50                      | 40.67                      | 1.45066            | 0.06771            |
| $RH_2C_2C_2C_2N$                                           | $C_b$ | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                                  | 0.91771                         | 0.81549                        | -16.68412                                | -16.60325                                  | 80.53                      | 99.47                      | 37.51                      | 1.51718            | 0.13423            |
| $C-H$ (CH <sub>3</sub> )                                   | C     | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                                  | 0.91771                         | 0.86359                        | -15.75493                                | -15.56407                                  | 77.49                      | 102.51                     | 41.48                      | 1.23564            | 0.18708            |
| $C-H$ (CH <sub>3</sub> )                                   | C     | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                                  | 0.91771                         | 0.81549                        | -16.68412                                | -16.60325                                  | 68.47                      | 111.53                     | 35.84                      | 1.35486            | 0.29933            |
| $C-H$ (CH <sub>3</sub> ) (ii)                              | C     | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                                  | 0.91771                         | 0.77247                        | -17.61330                                | -17.42244                                  | 61.10                      | 118.90                     | 31.37                      | 1.42988            | 0.37226            |
| $H_2C_2C_2H_2CH_2-$<br>(C-C (a))                           | $C_u$ | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                                  | 0.91771                         | 0.86359                        | -15.75493                                | -15.56407                                  | 63.82                      | 116.18                     | 30.68                      | 1.83879            | 0.38106            |
| $H_2C_2C_2H_2CH_2-$<br>(C-C (a))                           | $C_b$ | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                                  | 0.91771                         | 0.81549                        | -16.68412                                | -16.60325                                  | 56.41                      | 123.59                     | 26.06                      | 1.90090            | 0.45117            |
| $R-H_2C_2C_2(H_2C_2-R')HCH_2-$<br>(C-C (b))                | $C_s$ | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                                  | 0.91771                         | 0.77247                        | -17.61330                                | -17.42244                                  | 48.30                      | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| $R-H_2C_2C_2(R''-H_2C_2)C_2(R''-H_2C_2)CH_2-$<br>(C-C (c)) | $C_h$ | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -154.71860                                                  | 0.91771                         | 0.73889                        | -17.92866                                | -17.73779                                  | 48.21                      | 131.79                     | 21.74                      | 1.95734            | 0.50570            |
| $isoC_2C_2(H_2C_2-R')HCH_2-$<br>(C-C (d))                  | $C_b$ | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                                  | 0.91771                         | 0.77247                        | -17.61330                                | -17.42244                                  | 48.30                      | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| $tertC_2C_2(R''-H_2C_2)C_2(R''-H_2C_2)CH_2-$<br>(C-C (e))  | $C_b$ | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.51399                                                  | 0.91771                         | 0.67655                        | -17.92866                                | -17.73779                                  | 50.04                      | 129.96                     | 22.66                      | 1.94462            | 0.49298            |
| $tertC_2C_2(H_2C_2-R')HCH_2-$<br>(C-C (f))                 | $C_b$ | -0.72457                | -0.92918                | -0.92918                | 0                       | -154.19863                                                  | 0.91771                         | 0.78155                        | -17.40869                                | -17.21783                                  | 52.78                      | 127.22                     | 24.04                      | 1.92443            | 0.47279            |
| $isoC_2C_2(R''-H_2C_2)C_2(R''-H_2C_2)CH_2-$<br>(C-C (f))   | $C_b$ | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.51399                                                  | 0.91771                         | 0.67655                        | -17.92866                                | -17.73779                                  | 50.04                      | 129.96                     | 22.66                      | 1.94462            | 0.49298            |

Table 15.144. The energy parameters (eV) of functional groups of nitriles.

| Parameters                                       | C-C (f)<br>Group | C-N<br>Group | C-H <sub>2</sub><br>Group | C-H <sub>3</sub><br>Group | C-H<br>Group   | C-C (a)<br>Group | C-C (b)<br>Group | C-C (c)<br>Group | C-C (d)<br>Group | C-C (e)<br>Group | C-C (f)<br>Group |
|--------------------------------------------------|------------------|--------------|---------------------------|---------------------------|----------------|------------------|------------------|------------------|------------------|------------------|------------------|
| $n_1$                                            | 1                | 3            | 2                         | 1                         | 1              | 1                | 1                | 1                | 1                | 1                | 1                |
| $n_2$                                            | 0                | 0            | 1                         | 0                         | 0              | 0                | 0                | 0                | 0                | 0                | 0                |
| $n_3$                                            | 0                | 0            | 0                         | 0                         | 0              | 0                | 0                | 0                | 0                | 0                | 0                |
| $C_1$                                            | 0.5              | 0.5          | 0.75                      | 0.75                      | 0.75           | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              |
| $C_2$                                            | 1                | 1            | 1                         | 1                         | 1              | 1                | 1                | 1                | 1                | 1                | 1                |
| $C_3$                                            | 1                | 1            | 1                         | 1                         | 1              | 1                | 1                | 1                | 1                | 1                | 1                |
| $C_4$                                            | 0.91771          | 0.91140      | 0.91771                   | 0.91771                   | 0.91771        | 0.91771          | 0.91771          | 0.91771          | 0.91771          | 0.91771          | 0.91771          |
| $C_5$                                            | 0                | 1            | 0                         | 1                         | 1              | 0                | 0                | 0                | 1                | 1                | 0                |
| $C_6$                                            | 2                | 6            | 1                         | 1                         | 1              | 2                | 2                | 2                | 2                | 2                | 2                |
| $C_7$                                            | 0                | 0            | 3                         | 1                         | 1              | 0                | 0                | 0                | 0                | 0                | 0                |
| $C_{10}$                                         | 0.5              | 0.5          | 0.75                      | 0.75                      | 0.75           | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              |
| $C_{20}$                                         | 1                | 1            | 1                         | 1                         | 1              | 1                | 1                | 1                | 1                | 1                | 1                |
| $V'_e$ (eV)                                      | -33.01231        | -207.49229   | -107.32728                | -70.41425                 | -35.12015      | -28.79214        | -28.79214        | -29.10112        | -28.79214        | -29.10112        | -29.10112        |
| $V'_p$ (eV)                                      | 9.83824          | 37.16984     | 38.92728                  | 25.78002                  | 12.87680       | 9.33352          | 9.33352          | 9.37273          | 9.33352          | 9.37273          | 9.37273          |
| $T$ (eV)                                         | 8.63043          | 86.03250     | 32.53914                  | 21.06675                  | 10.48582       | 6.77464          | 6.77464          | 6.90500          | 6.77464          | 6.90500          | 6.90500          |
| $V'_m$ (eV)                                      | -4.31522         | -43.01625    | -16.26957                 | -10.53337                 | -5.24291       | -3.38732         | -3.38732         | -3.45250         | -3.38732         | -3.45250         | -3.45250         |
| $E'_{(100\text{ m})}$ (eV)                       | -14.63489        | 32.40004     | -15.56407                 | -15.56407                 | -14.63489      | -15.56407        | -15.56407        | -15.35946        | -15.56407        | -15.35946        | -15.35946        |
| $\Delta E'_{(100\text{ m})}$ (eV)                | -1.85837         | 0            | 0                         | 0                         | 0              | 0                | 0                | 0                | 0                | 0                | 0                |
| $E'_T$ (eV)                                      | -12.77652        | 32.40004     | -15.56407                 | -15.56407                 | -14.63489      | -15.56407        | -15.56407        | -15.35946        | -15.56407        | -15.35946        | -15.35946        |
| $E'_T$ (eV)                                      | -31.63537        | -94.90616    | -67.69451                 | -49.66493                 | -31.63533      | -31.63537        | -31.63537        | -31.63535        | -31.63537        | -31.63535        | -31.63535        |
| $E'_T$ (atom - atom, msp <sup>3</sup> , AO) (eV) | -1.85836         | -1.56513     | 0                         | 0                         | 0              | -1.85836         | -1.85836         | -1.44915         | -1.85836         | -1.44915         | -1.44915         |
| $E'_T$ (100) (eV)                                | -33.49374        | -96.47124    | -67.69450                 | -49.66493                 | -31.63537      | -33.49373        | -33.49373        | -33.08452        | -33.49373        | -33.08452        | -33.08452        |
| $\omega$ (10 <sup>4</sup> rad/s)                 | 19.2516          | 22.0753      | 24.9286                   | 24.2751                   | 24.1759        | 9.43699          | 9.43699          | 15.4846          | 9.43699          | 9.55643          | 9.55643          |
| $E'_K$ (eV)                                      | 12.67172         | 14.53031     | 16.40846                  | 15.97831                  | 15.91299       | 6.21159          | 6.21159          | 10.19220         | 6.21159          | 6.29021          | 6.29021          |
| $E'_D$ (eV)                                      | -0.23588         | -0.24250     | -0.25352                  | -0.25017                  | -0.24966       | -0.16515         | -0.16515         | -0.20896         | -0.16515         | -0.16416         | -0.16416         |
| $E'_{K10}$ (eV)                                  | 0.11407          | 0.28107      | 0.35532                   | 0.35532                   | 0.35532        | 0.12312          | 0.17978          | 0.09944          | 0.12312          | 0.12312          | 0.12312          |
| $E'_{K10}$ (Eq. (13.458))                        | [37]             | [37]         | (Eq. (13.458))            | (Eq. (13.458))            | (Eq. (13.458)) | [2]              | [4]              | [5]              | [2]              | [2]              | [2]              |
| $E'_{K10}$ (Eq. (13.458))                        | -0.17884         | -0.10197     | -0.22757                  | -0.14502                  | -0.07200       | -0.10359         | -0.07526         | -0.15924         | -0.10359         | -0.10260         | -0.10260         |
| $E'_{K10}$ (eV)                                  | 0.14803          | 0.14185      | 0.14803                   | 0.14803                   | 0.14803        | 0.14803          | 0.14803          | 0.14803          | 0.14803          | 0.14803          | 0.14803          |
| $E'_T$ (group) (eV)                              | -33.67258        | -96.77713    | -67.92207                 | -49.80996                 | -31.70737      | -33.59732        | -33.49373        | -33.24376        | -33.59732        | -33.18712        | -33.18712        |
| $E'_{K10}$ (Eq. (13.458))                        | -14.63489        | -14.63489    | -14.63489                 | -14.63489                 | -14.63489      | -14.63489        | -14.63489        | -14.63489        | -14.63489        | -14.63489        | -14.63489        |
| $E'_{K10}$ (Eq. (13.458))                        | 0                | 0            | -13.59844                 | -13.59844                 | -13.59844      | 0                | 0                | 0                | 0                | 0                | 0                |
| $E'_{K10}$ (eV)                                  | 4.40280          | 8.82594      | 12.49186                  | 7.83016                   | 3.32601        | 4.32754          | 4.29921          | 3.97398          | 4.17951          | 3.62128          | 3.91734          |





# THIOLS ( $C_nH_{2n+2}S_m$ , $n=1,2,3,4,5\ldots\infty$ )

The alkyl thiols,  $C_nH_{2n+2}S_m$ , comprise a  $SH$  functional group and a  $C-S$  functional group. The alkyl portion of the alkyl thiol may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The  $n$ -alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and  $t$ -butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to  $t$ -butyl, and  $t$ -butyl to  $t$ -butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in thiols are equivalent to those in branched-chain alkanes.

The parameters of the  $SH$  functional group is solved using Eq. (15.41). As in the case of the  $C-H$  bonds of  $CH_n$ ,  $n=1,2,3$ , the  $S-H$ -bond MO is a partial prolate spheroid in between the sulfur and hydrogen nuclei and is continuous with the  $S3p$  shell. The energy of the  $H_2$ -type ellipsoidal MO is matched to that of the  $S3p$  shell and comprises 75% of a  $H_2$ -type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. Since the energy of  $S$ ,  $E(S) = -10.36001 \text{ eV}$ , is less than that of  $H$ , the linear combination of the  $H_2$ -type ellipsoidal MO with the  $S3p$  shell further comprises an excess 50% charge-density donation from  $H$  to the  $S3p$  shell of the  $S-H$ -bond MO to achieve an energy minimum. The initial total energy of the shell is given by the sum over the four  $3p$  electrons. From Eq. (15.12), the sum  $E_T(S, 3p)$  of the energies of  $S$ ,  $S^+$ ,  $S^{2+}$ , and  $S^{3+}$  [38] is

$$\begin{aligned} E_T(S, 3p) &= 10.36001 \text{ eV} + 23.33788 \text{ eV} + 34.79 \text{ eV} + 47.222 \text{ eV} \\ &= 115.70989 \text{ eV} \end{aligned} \quad (15.118)$$

By considering that the central field decreases by an integer for each successive electron of the shell, the radius  $r_{3p}$  of the  $S3p$  shell may be calculated from the Coulombic energy using Eqs. (15.13) and (15.118):

$$r_{3p} = \sum_{q=12}^{15} \frac{(Z-q)e^2}{8\pi\epsilon_0 (e115.70989 \text{ eV})} = \frac{10e^2}{8\pi\epsilon_0 (e115.70989 \text{ eV})} = 1.17585a_0 \quad (15.119)$$

where  $Z=16$  for sulfur. Using Eqs. (15.14) and (15.119), the Coulombic energy  $E_{Coulomb}(S, 3p)$  of the outer electron of the  $S3p$  shell is

$$E_{Coulomb}(S, 3p) = \frac{-e^2}{8\pi\epsilon_0 r_{3p}} = \frac{-e^2}{8\pi\epsilon_0 1.17585a_0} = -11.57099 \text{ eV} \quad (15.120)$$

The sharing of the electrons between the  $S$  and  $H$  atoms permits the formation an  $S-H$ -bond MO that is lowered more in energy than the participating  $S3p$  orbital which consequently increases in energy. By considering the 50% electron redistribution in the  $S-H$  group as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius  $r_{S-H3p}$  of the  $S3p$  shell may be calculated from the Coulombic energy using Eq. (15.18)

$$\begin{aligned} r_{S-H3p} &= \left( \sum_{n=12}^{15} (Z-n) + 0.25 \right) \frac{e^2}{8\pi\epsilon_0 (e115.70989 \text{ eV})} \\ &= \frac{10.5e^2}{8\pi\epsilon_0 (e115.70989 \text{ eV})} \\ &= 1.23465a_0 \end{aligned} \quad (15.121)$$

where the  $s = -1$  in Eq. (15.18) due to the charge donation from  $H$  to  $S$ . Using Eqs. (15.19) and (15.121), the Coulombic energy  $E_{Coulomb}(S_{S-H}, 3p)$  of the outer electron of the  $S3p$  shell is

$$\begin{aligned} E_{Coulomb}(S_{S-H}, 3p) &= \frac{-e^2}{8\pi\epsilon_0 r_{S-H3p}} \\ &= \frac{-e^2}{8\pi\epsilon_0 1.23465a_0} \\ &= -11.01999 \text{ eV} \end{aligned} \quad (15.122)$$

Thus,  $E_r(S-H, 3p)$ , the energy change of each  $S3p$  shell with the formation of the  $S-H$ -bond MO is given by the difference between Eq. (15.120) and Eq. (15.122):

$$\begin{aligned} E_r(S-H, 3p) &= E(S_{S-H}, 3p) - E(S, 3p) \\ &= -11.01999 \text{ eV} - (-11.57099 \text{ eV}) \\ &= 0.55100 \text{ eV} \end{aligned} \quad (15.123)$$

15 Then, in Eq. (15.42):

$$\begin{aligned} E_r(AO / HO) &= E(S) - E_r(S-H, 3p) \\ &= -10.36001 \text{ eV} - 0.55100 \text{ eV} \\ &= -10.91101 \text{ eV} \end{aligned} \quad (15.124)$$

And, in Eq. (15.56),

$$E_r(\text{atom} - \text{atom}, msp^3.AO) = 0.55100 \text{ eV} \quad (15.125)$$

Due to the charge donation from  $H$  to  $S$ ,  $c_1 = 1$  in both Eqs. (15.42) and (15.56). As in the case of the  $C-H$ -bond MO,  $C_1 = 0.75$  based on the orbital composition. In alkyl thiols, the energy of sulfur is less than the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). Thus,  $c_2$  in Eq. (15.52) is also one, and the energy matching condition is  
 5 determined by the  $C_2$  parameter. Using the energy of  $S$ ,  $E(S) = -10.36001 \text{ eV}$  in Eq. (15.65), the hybridization factor  $C_2$  of Eq. (15.52) for the  $S-H$ -bond MO is

$$C_2(S3p \text{ to } H) = \frac{E(S, 3p)}{E(H)} = \frac{-10.36001 \text{ eV}}{-13.60580 \text{ eV}} = 0.76144 \quad (15.126)$$

Since the energy of  $S$  is matched to the Coulombic energy between the electron and proton of  $H$ ,  

$$E(H(a_0)), \quad E_{\text{initial}}(c_s \text{ AO/HO}) = E(H(a_0)) = -13.60580 \text{ eV},$$
  
 10  $E_{\text{initial}}(c_s \text{ AO/HO}) = E(H) = -13.59844 \text{ eV}$ , and  $E_{\text{mag}}$  is that corresponding to  $E(H(a_0))$  given by Eq. (15.58).  $E_D(\text{Group})$  for hydrogen sulfide is equivalent to that of the  $SH$  functional group, and the  $E_D(\text{Group})$  (eV) for dihydrogen sulfide follows the same derivation as that for the  $SH$  functional group except that the parameters correspond to  $n_1 = 2$  rather than  $n_1 = 1$  in Eqs. (15.42) and (15.56).

15 Furthermore, with the energy of  $S$  matched to the Coulombic energy between the electron and proton of  $H$ , the energy of the  $C-S$ -bond MO is the sum of the component energies of the  $H_2$ -type ellipsoidal MO given in Eq. (15.42) with  $E(\text{AO/HO}) = 0$  and  $E_T(\text{AO/HO}) = \Delta E_{H_2 \text{ MO}}(\text{AO/HO})$ . Then, the solution of the  $C-S$  functional group comprises the hybridization of the  $2s$  and  $2p$  AOs of  $C$  to form a single  $2sp^3$  shell as an  
 20 energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the  $S$  AO to form a MO permits each participating orbital to decrease in radius and energy. Since the energy of sulfur is less than the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243),  $c_2$  in Eq. (15.52) is one, and the energy matching condition is determined by the  $C_2$  parameter. Then,  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a  
 25 corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)), and the  $S$  AO has an energy of  $E(S) = -10.36001 \text{ eV}$ . To meet the equipotential condition of the union of the

$C-S$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $C_2$  of Eq. (15.51) for the  $C-S$ -bond MO given by Eqs. (15.68) and (15.70) is

$$C_2(C2sp^3HO \text{ to } S) = \frac{E(S)}{E(C, 2sp^3)} c_2(C2sp^3HO) = \frac{-10.36001 \text{ eV}}{-14.63489 \text{ eV}} (0.91771) = 0.64965 \quad (15.127)$$

Since the sulfur is energy matched to  $E(H(a_0))$  in the  $S-H$ -bond MO,

5  $E_T(atom - atom, msp^3.AO)$  of the  $C-S$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $S$  atoms to the MO is  $-0.72457 \text{ eV}$  corresponding to the energy contribution equivalent to that of a methyl group (Eq. (14.151)).

The symbols of the functional groups of branched-chain alkyl thiols are given in Table 15.147. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and  
10 energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl thiols are given in Tables 15.148, 15.149, and 15.150, respectively. The total energy of each alkyl thiol given in Table 15.151 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.150 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted  
15 from the weighted sum of the  $E_D(Group)$  ( $\text{eV}$ ) values based on composition is given by Eq. (15.58). The  $C-C$  bonds to the  $HCSH$  group (one  $H$  bond to  $C$ ) were each treated as an iso  $C-C$  bond. The  $C-C$  bonds to the  $CSH$  group (no  $H$  bonds to  $C$ ) were each treated as a tert-butyl  $C-C$ .  $E_{mag}$  was subtracted for each t-butyl group. The bond angle parameters of alkyl thiols determined using Eqs. (15.79-15.108) are given in Table 15.152.

Table 15.147. The symbols of functional groups of alkyl thiols.

| Functional Group      | SH Group Symbol        |
|-----------------------|------------------------|
| SH group              | SH                     |
| H <sub>2</sub> S      | H <sub>2</sub> S       |
| C-S                   | C-S                    |
| CH <sub>3</sub> group | C-H (CH <sub>3</sub> ) |
| CH <sub>2</sub> group | C-H (CH <sub>2</sub> ) |
| CH                    | C-H                    |
| CC bond (n-C)         | C-C (a)                |
| CC bond (iso-C)       | C-C (b)                |
| CC bond (tert-C)      | C-C (c)                |
| CC (iso to iso-C)     | C-C (d)                |
| CC (t to t-C)         | C-C (e)                |
| CC (t to iso-C)       | C-C (f)                |

Table 15.148. The geometrical bond parameters of alkyl thiols and experimental values [1].

| Parameter               | S-H (H <sub>2</sub> S)       | SH Group                  | C-S Group              | C-H (CH <sub>3</sub> ) Group | C-H (CH <sub>2</sub> ) Group | C-H Group            | C-C (a) Group      | C-C (b) Group      | C-C (c) Group      | C-C (d) Group      | C-C (e) Group      | C-C (f) Group      |
|-------------------------|------------------------------|---------------------------|------------------------|------------------------------|------------------------------|----------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| $a$ (Å)                 | 1.83762                      | 1.83762                   | 1.90975                | 1.64920                      | 1.67122                      | 1.67465              | 2.12499            | 2.12499            | 2.10725            | 2.12499            | 2.10725            | 2.10725            |
| $c'$ (Å)                | 1.26842                      | 1.26842                   | 1.71455                | 1.04856                      | 1.05535                      | 1.05661              | 1.45744            | 1.45744            | 1.45164            | 1.45744            | 1.45164            | 1.45164            |
| Bond Length<br>2c' (Å)  | 1.34244                      | 1.34244                   | 1.81460                | 1.10974                      | 1.11713                      | 1.11827              | 1.54280            | 1.54280            | 1.53635            | 1.54280            | 1.53635            | 1.53635            |
| Exp. Bond Length<br>(Å) | 1.3556<br>(hydrogen sulfide) | 1.34066<br>(methanethiol) | 1.819<br>(ethanethiol) | 1.107<br>(C-H propane)       | 1.107<br>(C-H propane)       | 1.122<br>(isobutane) | 1.532<br>(propane) | 1.532<br>(propane) | 1.532<br>(propane) | 1.532<br>(propane) | 1.532<br>(propane) | 1.532<br>(propane) |
| $b, c$ (Å)              | 1.32964                      | 1.32964                   | 0.84112                | 1.117<br>(C-H butane)        | 1.117<br>(C-H butane)        | 1.29924              | 1.531<br>(butane)  | 1.531<br>(butane)  | 1.531<br>(butane)  | 1.531<br>(butane)  | 1.531<br>(butane)  | 1.531<br>(butane)  |
| $e$                     | 0.69025                      | 0.69025                   | 0.89778                | 1.27295                      | 1.29569                      | 0.63095              | 1.54616            | 1.54616            | 1.52750            | 1.54616            | 1.52750            | 1.52750            |
|                         |                              |                           |                        | 0.63580                      | 0.63159                      |                      | 0.68600            | 0.68600            | 0.68888            | 0.68600            | 0.68888            | 0.68888            |

Table 15.149. The MO to HO intercept geometrical bond parameters of alkyl thiols.  $R, R', R''$  are H or alkyl groups.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{resp. } A.O.)$ .

| Bond                                                                                                                       | Atom           | $E_T$<br>(eV)<br>Bond 1 | $E_T$<br>(eV)<br>Bond 2 | $E_T$<br>(eV)<br>Bond 3 | $E_T$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>(eV) | $r_{\text{final}}$<br>( $a_0$ ) | $r_{\text{final}}$<br>( $a_0$ ) | $E_{\text{total}}^{\text{bond}}$<br>(eV)<br>Final | $E(C2sp^3)$<br>(eV)<br>Final | $\theta'$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | $d_1$<br>( $a_0$ ) | $d_2$<br>( $a_0$ ) |
|----------------------------------------------------------------------------------------------------------------------------|----------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------------|---------------------------------|---------------------------------|---------------------------------------------------|------------------------------|---------------------------|----------------------------|----------------------------|--------------------|--------------------|
| S-H<br>(hydrogen sulfide)                                                                                                  | S              | 0.55100                 | 0                       | 0                       | 0                       |                               | 1.32010                         | 1.23465                         | -11.01999                                         |                              | 108.65                    | 71.35                      | 61.62                      | 0.87355            | 0.39487            |
| RS-H<br>(dihydrogen sulfide)                                                                                               | S              | -0.30229                | 0.55100                 | 0                       | 0                       |                               | 1.32010                         | 0.92955                         | -14.63704                                         |                              | 87.09                     | 92.91                      | 44.28                      | 1.31557            | 0.04714            |
| C-H <sub>3</sub> -SH                                                                                                       | S              | -0.30229                | 0.55100                 | 0                       | 0                       |                               | 1.32010                         | 0.92955                         | -14.63704                                         |                              | 132.06                    | 47.94                      | 55.13                      | 1.09181            | 0.62274            |
| C <sub>1</sub> H <sub>3</sub> -SH                                                                                          | C <sub>1</sub> | -0.30229                | 0                       | 0                       | 0                       | -151.97798                    | 0.91771                         | 0.89382                         | -15.18804                                         | -14.99117                    | 69.84                     | 110.16                     | 88.87                      | 0.03762            | 1.67692            |
| RC <sub>1</sub> H <sub>3</sub> C <sub>2</sub> H <sub>5</sub> -C <sub>1</sub> H <sub>3</sub> SH                             | C <sub>1</sub> | -0.30229                | -0.92918                | 0                       | 0                       | -152.90716                    | 0.91771                         | 0.84418                         | -16.11722                                         | -15.92636                    | 128.69                    | 51.31                      | 51.57                      | 1.18689            | 0.32765            |
| C-H (CH <sub>3</sub> )                                                                                                     | C              | -0.92918                | 0                       | 0                       | 0                       | -152.54487                    | 0.91771                         | 0.86359                         | -15.75493                                         | -15.56407                    | 77.49                     | 102.51                     | 41.48                      | 1.23564            | 0.18708            |
| C-H (CH <sub>2</sub> )                                                                                                     | C              | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                    | 0.91771                         | 0.81549                         | -16.68412                                         | -16.49325                    | 68.47                     | 111.53                     | 35.84                      | 1.35486            | 0.29933            |
| C-H (CH)                                                                                                                   | C              | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                    | 0.91771                         | 0.77247                         | -17.61330                                         | -17.42244                    | 61.10                     | 118.90                     | 31.37                      | 1.42988            | 0.37326            |
| H <sub>3</sub> C <sub>1</sub> C <sub>2</sub> H <sub>5</sub> (H <sub>2</sub> -)                                             | C <sub>1</sub> | -0.92918                | 0                       | 0                       | 0                       | -152.54487                    | 0.91771                         | 0.86359                         | -15.75493                                         | -15.56407                    | 63.82                     | 116.18                     | 30.08                      | 1.83879            | 0.38106            |
| (C-C (eq))                                                                                                                 | C <sub>1</sub> | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                    | 0.91771                         | 0.81549                         | -16.68412                                         | -16.49325                    | 56.41                     | 123.59                     | 26.06                      | 1.90890            | 0.45117            |
| R-H <sub>3</sub> C <sub>1</sub> (R'-H <sub>3</sub> C <sub>2</sub> )(R''-H <sub>3</sub> C <sub>3</sub> )HCH <sub>2</sub> -  | C <sub>1</sub> | -0.92918                | -0.92918                | 0                       | 0                       | -154.40324                    | 0.91771                         | 0.77247                         | -17.61330                                         | -17.42244                    | 48.30                     | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| R-H <sub>3</sub> C <sub>1</sub> (R'-H <sub>3</sub> C <sub>2</sub> )(R''-H <sub>3</sub> C <sub>3</sub> )(CH <sub>2</sub> -) | C <sub>1</sub> | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.71860                    | 0.91771                         | 0.73889                         | -17.92866                                         | -17.73779                    | 48.21                     | 131.79                     | 21.74                      | 1.95734            | 0.50370            |
| (C-C (eq))                                                                                                                 | C <sub>1</sub> | -0.92918                | -0.92918                | -0.92918                | -0.72457                | -154.71860                    | 0.91771                         | 0.73889                         | -17.92866                                         | -17.73779                    | 48.21                     | 131.79                     | 21.74                      | 1.95734            | 0.50370            |
| isoC <sub>1</sub> C <sub>2</sub> (H <sub>3</sub> C <sub>3</sub> -R')HCH <sub>2</sub> -                                     | C <sub>1</sub> | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                    | 0.91771                         | 0.77247                         | -17.61330                                         | -17.42244                    | 48.30                     | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| (C-C (eq))                                                                                                                 | C <sub>1</sub> | -0.92918                | -0.92918                | -0.92918                | -0.72457                | -154.40324                    | 0.91771                         | 0.77247                         | -17.61330                                         | -17.42244                    | 48.30                     | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| isoC <sub>1</sub> (R'-H <sub>3</sub> C <sub>2</sub> )(R''-H <sub>3</sub> C <sub>3</sub> )CH <sub>2</sub> -                 | C <sub>1</sub> | -0.72457                | -0.92918                | -0.72457                | -0.72457                | -154.51399                    | 0.91771                         | 0.76765                         | -17.92866                                         | -17.73779                    | 50.04                     | 129.96                     | 22.66                      | 1.94462            | 0.49298            |
| (C-C (eq))                                                                                                                 | C <sub>1</sub> | -0.72457                | -0.92918                | -0.72457                | -0.72457                | -154.51399                    | 0.91771                         | 0.76765                         | -17.92866                                         | -17.73779                    | 50.04                     | 129.96                     | 22.66                      | 1.94462            | 0.49298            |
| isoC <sub>1</sub> C <sub>2</sub> (H <sub>3</sub> C <sub>3</sub> -R')HCH <sub>2</sub> -                                     | C <sub>1</sub> | -0.72457                | -0.92918                | -0.92918                | 0                       | -154.19863                    | 0.91771                         | 0.78155                         | -17.40869                                         | -17.21783                    | 52.78                     | 127.22                     | 24.04                      | 1.93445            | 0.47279            |
| (C-C (eq))                                                                                                                 | C <sub>1</sub> | -0.72457                | -0.92918                | -0.92918                | -0.72457                | -154.19863                    | 0.91771                         | 0.78155                         | -17.40869                                         | -17.21783                    | 52.78                     | 127.22                     | 24.04                      | 1.93445            | 0.47279            |
| isoC <sub>1</sub> (R'-H <sub>3</sub> C <sub>2</sub> )(R''-H <sub>3</sub> C <sub>3</sub> )CH <sub>2</sub> -                 | C <sub>1</sub> | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.51399                    | 0.91771                         | 0.76765                         | -17.92866                                         | -17.73779                    | 50.04                     | 129.96                     | 22.66                      | 1.94462            | 0.49298            |
| (C-C (eq))                                                                                                                 | C <sub>1</sub> | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.51399                    | 0.91771                         | 0.76765                         | -17.92866                                         | -17.73779                    | 50.04                     | 129.96                     | 22.66                      | 1.94462            | 0.49298            |

Table I.5.150. The energy parameters (eV) of functional groups of alkyl thiols.

| Parameters                  | $H_{1s}$   | $SH$      | $C-S$     | $C-H$      | $C-H_2$   | $C-H_3$   | $C-C$     | $C-C$     | $C-C$     | $C-C$     | $C-C$     | $C-C$     |
|-----------------------------|------------|-----------|-----------|------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
|                             | Group      | Group     | Group     | Group      | Group     | Group     | Group     | Group     | Group     | Group     | Group     | Group     |
| $H_1$                       | 2          | 1         | 1         | 1          | 2         | 3         | 1         | 1         | 1         | 1         | 1         | 1         |
| $H_2$                       | 0          | 0         | 0         | 0          | 1         | 2         | 0         | 0         | 0         | 0         | 0         | 0         |
| $H_3$                       | 0          | 0         | 0         | 0          | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 0         |
| $C_1$                       | 0.75       | 0.75      | 0.5       | 0.75       | 0.75      | 0.75      | 0.75      | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       |
| $C_2$                       | 0.76144    | 0.76144   | 0.64965   | 1          | 1         | 1         | 1         | 1         | 1         | 1         | 1         | 1         |
| $C_3$                       | 1          | 1         | 1         | 1          | 1         | 1         | 1         | 1         | 1         | 1         | 1         | 1         |
| $C_4$                       | 1          | 1         | 1         | 0.91771    | 0.91771   | 0.91771   | 0.91771   | 0.91771   | 0.91771   | 0.91771   | 0.91771   | 0.91771   |
| $C_5$                       | 2          | 1         | 0         | 1          | 1         | 0         | 0         | 0         | 0         | 0         | 0         | 0         |
| $C_6$                       | 1          | 1         | 2         | 1          | 1         | 1         | 2         | 2         | 2         | 2         | 2         | 2         |
| $C_7$                       | 1          | 1         | 0         | 1          | 2         | 3         | 0         | 0         | 0         | 0         | 0         | 0         |
| $C_{10}$                    | 0.75       | 0.75      | 0.5       | 0.75       | 0.75      | 0.75      | 0.75      | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       |
| $C_{11}$                    | 0.76144    | 0.76144   | 0.64965   | 1          | 1         | 1         | 1         | 1         | 1         | 1         | 1         | 1         |
| $V_1$ (eV)                  | -72.80662  | -36.40331 | -46.36495 | -107.32728 | -70.41425 | -55.12015 | -28.79214 | -28.79214 | -28.79214 | -28.79214 | -28.79214 | -28.79214 |
| $V_2$ (eV)                  | 21.43310   | 10.72655  | 7.93551   | 38.92728   | 25.78002  | 12.87680  | 9.33552   | 9.33552   | 9.33552   | 9.33552   | 9.33552   | 9.33552   |
| $T$ (eV)                    | 19.81003   | 9.90502   | 12.13899  | 32.53914   | 21.06675  | 10.48582  | 6.77464   | 6.77464   | 6.77464   | 6.77464   | 6.77464   | 6.77464   |
| $V_3$ (eV)                  | -9.90502   | -4.95251  | -6.00949  | -16.26957  | -10.53337 | -5.24291  | -3.38732  | -3.38732  | -3.38732  | -3.38732  | -3.38732  | -3.38732  |
| $E_{1st}^{ion} (eV)$        | -20.72002  | -10.36001 | 0         | -15.56407  | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 |
| $\Delta E_{1st}^{ion} (eV)$ | 1.10200    | 0.55100   | -0.72457  | 0          | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 0         |
| $E_{1st}^{ion} (eV)$        | -19.61802  | -10.91101 | 0.72457   | -15.56407  | -15.56407 | -14.63489 | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 |
| $E_{2nd}^{ion} (eV)$        | -63.27032  | -31.63526 | -31.63537 | -67.69451  | -49.66493 | -31.63553 | -31.63557 | -31.63557 | -31.63557 | -31.63557 | -31.63557 | -31.63557 |
| $E_{3rd}^{ion} (eV)$        | 1.10200    | 0.55100   | -0.72457  | 0          | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 0         |
| $E_{4th}^{ion} (eV)$        | -62.16874  | -31.08437 | -32.35904 | -67.69450  | -49.66493 | -31.63557 | -31.63557 | -31.63557 | -31.63557 | -31.63557 | -31.63557 | -31.63557 |
| $\omega$ ( $10^5$ rad/s)    | 12.5415    | 12.5415   | 30.5436   | 24.9286    | 24.2751   | 24.1759   | 24.1759   | 24.1759   | 24.1759   | 24.1759   | 24.1759   | 24.1759   |
| $E_K$ (eV)                  | 8.25504    | 8.25504   | 20.10434  | 16.40846   | 15.97831  | 15.91299  | 15.91299  | 15.91299  | 15.91299  | 15.91299  | 15.91299  | 15.91299  |
| $E_{1st}^{exc}$ (eV)        | -0.17669   | -0.17669  | -0.28705  | -0.25352   | -0.25017  | -0.24966  | -0.16515  | -0.16515  | -0.16515  | -0.16515  | -0.16515  | -0.16515  |
| $E_{2nd}^{exc}$ (eV)        | 0.32422    | 0.32422   | 0.08146   | 0.35532    | 0.35532   | 0.35532   | 0.12312   | 0.12312   | 0.12312   | 0.12312   | 0.12312   | 0.12312   |
| $E_{3rd}^{exc}$ (eV)        | -0.01458   | -0.01458  | -0.24632  | -0.22757   | -0.14502  | -0.07200  | -0.10559  | -0.10559  | -0.10559  | -0.10559  | -0.10559  | -0.10559  |
| $E_{4th}^{exc}$ (eV)        | 0.11441    | 0.11441   | 0.14803   | 0.14803    | 0.14803   | 0.14803   | 0.14803   | 0.14803   | 0.14803   | 0.14803   | 0.14803   | 0.14803   |
| $E_{5th}^{exc}$ (eV)        | -31.10493a | -31.09296 | -32.60626 | -67.92207  | -49.80996 | -31.70737 | -33.59732 | -33.59732 | -33.59732 | -33.59732 | -33.59732 | -33.59732 |
| $E_{6th}^{exc}$ (eV)        | -13.60580  | -13.60580 | -14.63489 | -14.63489  | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{7th}^{exc}$ (eV)        | -13.59844  | -13.59844 | 0         | -13.59844  | -13.59844 | -13.59844 | 0         | 0         | 0         | 0         | 0         | 0         |
| $E_{8th}^{exc}$ (eV)        | 3.78628    | 3.77430   | 3.33648   | 12.49186   | 7.83016   | 3.32601   | 4.32754   | 4.29921   | 4.29921   | 4.29921   | 4.29921   | 4.29921   |
| $E_{9th}^{exc}$ (eV)        | -31.09296  | -31.09296 | -32.60626 | -67.92207  | -49.80996 | -31.70737 | -33.59732 | -33.59732 | -33.59732 | -33.59732 | -33.59732 | -33.59732 |
| $E_{10th}^{exc}$ (eV)       | -13.60580  | -13.60580 | -14.63489 | -14.63489  | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{11th}^{exc}$ (eV)       | -13.59844  | -13.59844 | 0         | -13.59844  | -13.59844 | -13.59844 | 0         | 0         | 0         | 0         | 0         | 0         |
| $E_{12th}^{exc}$ (eV)       | 3.78628    | 3.77430   | 3.33648   | 12.49186   | 7.83016   | 3.32601   | 4.32754   | 4.29921   | 4.29921   | 4.29921   | 4.29921   | 4.29921   |
| $E_{13th}^{exc}$ (eV)       | -31.09296  | -31.09296 | -32.60626 | -67.92207  | -49.80996 | -31.70737 | -33.59732 | -33.59732 | -33.59732 | -33.59732 | -33.59732 | -33.59732 |
| $E_{14th}^{exc}$ (eV)       | -13.60580  | -13.60580 | -14.63489 | -14.63489  | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{15th}^{exc}$ (eV)       | -13.59844  | -13.59844 | 0         | -13.59844  | -13.59844 | -13.59844 | 0         | 0         | 0         | 0         | 0         | 0         |
| $E_{16th}^{exc}$ (eV)       | 3.78628    | 3.77430   | 3.33648   | 12.49186   | 7.83016   | 3.32601   | 4.32754   | 4.29921   | 4.29921   | 4.29921   | 4.29921   | 4.29921   |
| $E_{17th}^{exc}$ (eV)       | -31.09296  | -31.09296 | -32.60626 | -67.92207  | -49.80996 | -31.70737 | -33.59732 | -33.59732 | -33.59732 | -33.59732 | -33.59732 | -33.59732 |
| $E_{18th}^{exc}$ (eV)       | -13.60580  | -13.60580 | -14.63489 | -14.63489  | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{19th}^{exc}$ (eV)       | -13.59844  | -13.59844 | 0         | -13.59844  | -13.59844 | -13.59844 | 0         | 0         | 0         | 0         | 0         | 0         |
| $E_{20th}^{exc}$ (eV)       | 3.78628    | 3.77430   | 3.33648   | 12.49186   | 7.83016   | 3.32601   | 4.32754   | 4.29921   | 4.29921   | 4.29921   | 4.29921   | 4.29921   |

a  $E_{1st}^{ion} (n=1,2,3) = E_{1st}^{ion} (n=1) - E_{2nd}^{ion} (n=1) = 62.19789 \text{ eV} - (-31.09296 \text{ eV})$ .

Table 15.151. The total bond energies of alkyl thiols calculated using the functional group composition and the energies of Table 15.150 compared to the experimental values [3]. The magnetic energy  $E_{\text{mag}}$  that is subtracted from the weighted sum of the  $E_p(\text{core})$  ( $\text{eV}$ ) values base composition is given by (15.58).

| Formula                                                                     | Name                        | $H_2S$ Group | $SH$ Group | $C-S$ Group | $CH_3$ | $CH_2$ | $CH$ | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | $E_{\text{mag}}$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|-----------------------------------------------------------------------------|-----------------------------|--------------|------------|-------------|--------|--------|------|-----------|-----------|-----------|-----------|-----------|-----------|------------------|-----------------------------------|-------------------------------------|----------------|
| $HS$                                                                        | Hydrogen Sulfide            | 1            | 1          | 0           | 0      | 0      | 0    | 0         | 0         | 0         | 0         | 0         | 0         | 0                | 3.7430                            | 3.633                               | -0.03320       |
| $CH_3S$                                                                     | Methylthiol                 | 0            | 1          | 0           | 0      | 0      | 0    | 0         | 0         | 0         | 0         | 0         | 0         | 0                | 7.5038                            | 7.603                               | 0.00082        |
| $CH_3CH_2S$                                                                 | Ethylthiol                  | 0            | 1          | 0           | 1      | 0      | 0    | 0         | 0         | 0         | 0         | 0         | 0         | 0                | 19.0264                           | 19.575                              | -0.00141       |
| $CH_3CH_2CH_2S$                                                             | 1-Propanethiol              | 0            | 1          | 0           | 1      | 1      | 0    | 0         | 0         | 0         | 0         | 0         | 0         | 0                | 31.7634                           | 31.762                              | 0.00005        |
| $CH_3CH_2CH_2CH_2S$                                                         | 2-Propanethiol              | 0            | 1          | 0           | 2      | 0      | 0    | 0         | 0         | 0         | 0         | 0         | 0         | 0                | 43.91804                          | 43.933                              | 0.00035        |
| $CH_3CH_2CH_2CH_2CH_2S$                                                     | 1-Butanethiol               | 0            | 1          | 0           | 2      | 1      | 0    | 0         | 0         | 0         | 0         | 0         | 0         | 0                | 56.0274                           | 56.089                              | 0.00063        |
| $CH_3CH_2CH_2CH_2CH_2CH_2S$                                                 | 2-Butanethiol               | 0            | 1          | 0           | 3      | 0      | 0    | 0         | 0         | 0         | 0         | 0         | 0         | 0                | 68.14830                          | 68.161                              | 0.00024        |
| $CH_3CH_2CH_2CH_2CH_2CH_2CH_2S$                                             | 2-Methyl-1-propanethiol     | 0            | 1          | 0           | 2      | 1      | 1    | 0         | 0         | 0         | 0         | 0         | 0         | 0                | 80.39114                          | 80.416                              | 0.00024        |
| $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2S$                                         | 2-Methyl-2-propanethiol     | 0            | 1          | 0           | 3      | 0      | 0    | 0         | 0         | 0         | 0         | 0         | 0         | 0                | 92.54884                          | 92.570                              | 0.00025        |
| $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2S$                                     | 2-Methyl-1-butanethiol      | 0            | 1          | 0           | 3      | 1      | 0    | 0         | 0         | 0         | 0         | 0         | 0         | 0                | 104.70000                         | 104.714                             | 0.00014        |
| $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2S$                                 | 1-Pentanethiol              | 0            | 1          | 0           | 4      | 0      | 0    | 0         | 0         | 0         | 0         | 0         | 0         | 0                | 116.85152                         | 116.881                             | -0.00094       |
| $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2S$                             | 2-Methyl-2-butanethiol      | 0            | 1          | 0           | 4      | 1      | 0    | 0         | 0         | 0         | 0         | 0         | 0         | 0                | 128.902194                        | 128.948                             | -0.00020       |
| $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2S$                         | 3-Methyl-2-butanethiol      | 0            | 1          | 0           | 5      | 0      | 0    | 0         | 0         | 0         | 0         | 0         | 0         | 0                | 140.95366                         | 140.984                             | -0.00094       |
| $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2S$                     | 2,2-Dimethyl-1-propanethiol | 0            | 1          | 0           | 3      | 1      | 0    | 0         | 0         | 0         | 0         | 0         | 0         | 0                | 152.99994                         | 153.024                             | -0.00024       |
| $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2S$                 | 1-Hexanethiol               | 0            | 1          | 0           | 5      | 0      | 0    | 0         | 0         | 0         | 0         | 0         | 0         | 0                | 165.05042                         | 165.081                             | -0.00094       |
| $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2S$             | 2-Methyl-2-pentanethiol     | 0            | 1          | 0           | 6      | 0      | 0    | 0         | 0         | 0         | 0         | 0         | 0         | 0                | 177.101902                        | 177.131                             | -0.00094       |
| $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2S$         | 2,3-Dimethyl-2-butanethiol  | 0            | 1          | 0           | 6      | 1      | 0    | 0         | 0         | 0         | 0         | 0         | 0         | 0                | 189.15238                         | 189.183                             | -0.00094       |
| $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2S$     | 1-Heptanethiol              | 0            | 1          | 0           | 6      | 0      | 0    | 0         | 0         | 0         | 0         | 0         | 0         | 0                | 201.20386                         | 201.234                             | -0.00094       |
| $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2S$ | 1-Octanethiol               | 0            | 1          | 0           | 7      | 0      | 0    | 0         | 0         | 0         | 0         | 0         | 0         | 0                | 213.25534                         | 213.286                             | -0.00094       |

Table 15.152. The bond angle parameters of alkyl thiols and experimental values [1]. In the calculation of  $\theta_i$ , the parameters from the preceding angle were used.  $E_i$  is  $E_i(\text{atom} - \text{atom}, \text{mp}, \text{AO})$ .

| Atoms of Angle | $2c_1$ Head 1 ( $a_0$ ) | $2c_2$ Head 2 ( $a_0$ ) | $2c_3$ Terminal Atoms ( $a_0$ ) | $E_{\text{calc}}^{\text{calc}}$ Atom 1 | Atom 1 Hybridization Designation (Table 13.3.A) | $E_{\text{calc}}^{\text{calc}}$ Atom 2 | Atom 2 Hybridization Designation (Table 13.3.A) | $c_1$ Atom 1 | $c_2$ Atom 2 | $c_3$ | $c_4$ | $c_5$ | $c_6$ | $c_7$ | $c_8$ | $c_9$ | $c_{10}$ | $c_{11}$ | $c_{12}$ | $c_{13}$ | $c_{14}$ | $c_{15}$ | $c_{16}$ | $c_{17}$ | $c_{18}$ | $c_{19}$ | $c_{20}$ | $c_{21}$ | $c_{22}$ | $c_{23}$ | $c_{24}$ | $c_{25}$ | $c_{26}$ | $c_{27}$ | $c_{28}$ | $c_{29}$ | $c_{30}$ | $c_{31}$ | $c_{32}$ | $c_{33}$ | $c_{34}$ | $c_{35}$ | $c_{36}$ | $c_{37}$ | $c_{38}$ | $c_{39}$ | $c_{40}$ | $c_{41}$ | $c_{42}$ | $c_{43}$ | $c_{44}$ | $c_{45}$ | $c_{46}$ | $c_{47}$ | $c_{48}$ | $c_{49}$ | $c_{50}$ | $c_{51}$ | $c_{52}$ | $c_{53}$ | $c_{54}$ | $c_{55}$ | $c_{56}$ | $c_{57}$ | $c_{58}$ | $c_{59}$ | $c_{60}$ | $c_{61}$ | $c_{62}$ | $c_{63}$ | $c_{64}$ | $c_{65}$ | $c_{66}$ | $c_{67}$ | $c_{68}$ | $c_{69}$ | $c_{70}$ | $c_{71}$ | $c_{72}$ | $c_{73}$ | $c_{74}$ | $c_{75}$ | $c_{76}$ | $c_{77}$ | $c_{78}$ | $c_{79}$ | $c_{80}$ | $c_{81}$ | $c_{82}$ | $c_{83}$ | $c_{84}$ | $c_{85}$ | $c_{86}$ | $c_{87}$ | $c_{88}$ | $c_{89}$ | $c_{90}$ | $c_{91}$ | $c_{92}$ | $c_{93}$ | $c_{94}$ | $c_{95}$ | $c_{96}$ | $c_{97}$ | $c_{98}$ | $c_{99}$ | $c_{100}$ | $c_{101}$ | $c_{102}$ | $c_{103}$ | $c_{104}$ | $c_{105}$ | $c_{106}$ | $c_{107}$ | $c_{108}$ | $c_{109}$ | $c_{110}$ | $c_{111}$ | $c_{112}$ | $c_{113}$ | $c_{114}$ | $c_{115}$ | $c_{116}$ | $c_{117}$ | $c_{118}$ | $c_{119}$ | $c_{120}$ | $c_{121}$ | $c_{122}$ | $c_{123}$ | $c_{124}$ | $c_{125}$ | $c_{126}$ | $c_{127}$ | $c_{128}$ | $c_{129}$ | $c_{130}$ | $c_{131}$ | $c_{132}$ | $c_{133}$ | $c_{134}$ | $c_{135}$ | $c_{136}$ | $c_{137}$ | $c_{138}$ | $c_{139}$ | $c_{140}$ | $c_{141}$ | $c_{142}$ | $c_{143}$ | $c_{144}$ | $c_{145}$ | $c_{146}$ | $c_{147}$ | $c_{148}$ | $c_{149}$ | $c_{150}$ | $c_{151}$ | $c_{152}$ | $c_{153}$ | $c_{154}$ | $c_{155}$ | $c_{156}$ | $c_{157}$ | $c_{158}$ | $c_{159}$ | $c_{160}$ | $c_{161}$ | $c_{162}$ | $c_{163}$ | $c_{164}$ | $c_{165}$ | $c_{166}$ | $c_{167}$ | $c_{168}$ | $c_{169}$ | $c_{170}$ | $c_{171}$ | $c_{172}$ | $c_{173}$ | $c_{174}$ | $c_{175}$ | $c_{176}$ | $c_{177}$ | $c_{178}$ | $c_{179}$ | $c_{180}$ | $c_{181}$ | $c_{182}$ | $c_{183}$ | $c_{184}$ | $c_{185}$ | $c_{186}$ | $c_{187}$ | $c_{188}$ | $c_{189}$ | $c_{190}$ | $c_{191}$ | $c_{192}$ | $c_{193}$ | $c_{194}$ | $c_{195}$ | $c_{196}$ | $c_{197}$ | $c_{198}$ | $c_{199}$ | $c_{200}$ | $c_{201}$ | $c_{202}$ | $c_{203}$ | $c_{204}$ | $c_{205}$ | $c_{206}$ | $c_{207}$ | $c_{208}$ | $c_{209}$ | $c_{210}$ | $c_{211}$ | $c_{212}$ | $c_{213}$ | $c_{214}$ | $c_{215}$ | $c_{216}$ | $c_{217}$ | $c_{218}$ | $c_{219}$ | $c_{220}$ | $c_{221}$ | $c_{222}$ | $c_{223}$ | $c_{224}$ | $c_{225}$ | $c_{226}$ | $c_{227}$ | $c_{228}$ | $c_{229}$ | $c_{230}$ | $c_{231}$ | $c_{232}$ | $c_{233}$ | $c_{234}$ | $c_{235}$ | $c_{236}$ | $c_{237}$ | $c_{238}$ | $c_{239}$ | $c_{240}$ | $c_{241}$ | $c_{242}$ | $c_{243}$ | $c_{244}$ | $c_{245}$ | $c_{246}$ | $c_{247}$ | $c_{248}$ | $c_{249}$ | $c_{250}$ | $c_{251}$ | $c_{252}$ | $c_{253}$ | $c_{254}$ | $c_{255}$ | $c_{256}$ | $c_{257}$ | $c_{258}$ | $c_{259}$ | $c_{260}$ | $c_{261}$ | $c_{262}$ | $c_{263}$ | $c_{264}$ | $c_{265}$ | $c_{266}$ | $c_{267}$ | $c_{268}$ | $c_{269}$ | $c_{270}$ | $c_{271}$ | $c_{272}$ | $c_{273}$ | $c_{274}$ | $c_{275}$ | $c_{276}$ | $c_{277}$ | $c_{278}$ | $c_{279}$ | $c_{280}$ | $c_{281}$ | $c_{282}$ | $c_{283}$ | $c_{284}$ | $c_{285}$ | $c_{286}$ | $c_{287}$ | $c_{288}$ | $c_{289}$ | $c_{290}$ | $c_{291}$ | $c_{292}$ | $c_{293}$ | $c_{294}$ | $c_{295}$ | $c_{296}$ | $c_{297}$ | $c_{298}$ | $c_{299}$ | $c_{300}$ | $c_{301}$ | $c_{302}$ | $c_{303}$ | $c_{304}$ | $c_{305}$ | $c_{306}$ | $c_{307}$ | $c_{308}$ | $c_{309}$ | $c_{310}$ | $c_{311}$ | $c_{312}$ | $c_{313}$ | $c_{314}$ | $c_{315}$ | $c_{316}$ | $c_{317}$ | $c_{318}$ | $c_{319}$ | $c_{320}$ | $c_{321}$ | $c_{322}$ | $c_{323}$ | $c_{324}$ | $c_{325}$ | $c_{326}$ | $c_{327}$ | $c_{328}$ | $c_{329}$ | $c_{330}$ | $c_{331}$ | $c_{332}$ | $c_{333}$ | $c_{334}$ | $c_{335}$ | $c_{336}$ | $c_{337}$ | $c_{338}$ | $c_{339}$ | $c_{340}$ | $c_{341}$ | $c_{342}$ | $c_{343}$ | $c_{344}$ | $c_{345}$ | $c_{346}$ | $c_{347}$ | $c_{348}$ | $c_{349}$ | $c_{350}$ | $c_{351}$ | $c_{352}$ | $c_{353}$ | $c_{354}$ | $c_{355}$ | $c_{356}$ | $c_{357}$ | $c_{358}$ | $c_{359}$ | $c_{360}$ | $c_{361}$ | $c_{362}$ | $c_{363}$ | $c_{364}$ | $c_{365}$ | $c_{366}$ | $c_{367}$ | $c_{368}$ | $c_{369}$ | $c_{370}$ | $c_{371}$ | $c_{372}$ | $c_{373}$ | $c_{374}$ | $c_{375}$ | $c_{376}$ | $c_{377}$ | $c_{378}$ | $c_{379}$ | $c_{380}$ | $c_{381}$ | $c_{382}$ | $c_{383}$ | $c_{384}$ | $c_{385}$ | $c_{386}$ | $c_{387}$ | $c_{388}$ | $c_{389}$ | $c_{390}$ | $c_{391}$ | $c_{392}$ | $c_{393}$ | $c_{394}$ | $c_{395}$ | $c_{396}$ | $c_{397}$ | $c_{398}$ | $c_{399}$ | $c_{400}$ | $c_{401}$ | $c_{402}$ | $c_{403}$ | $c_{404}$ | $c_{405}$ | $c_{406}$ | $c_{407}$ | $c_{408}$ | $c_{409}$ | $c_{410}$ | $c_{411}$ | $c_{412}$ | $c_{413}$ | $c_{414}$ | $c_{415}$ | $c_{416}$ | $c_{417}$ | $c_{418}$ | $c_{419}$ | $c_{420}$ | $c_{421}$ | $c_{422}$ | $c_{423}$ | $c_{424}$ | $c_{425}$ | $c_{426}$ | $c_{427}$ | $c_{428}$ | $c_{429}$ | $c_{430}$ | $c_{431}$ | $c_{432}$ | $c_{433}$ | $c_{434}$ | $c_{435}$ | $c_{436}$ | $c_{437}$ | $c_{438}$ | $c_{439}$ | $c_{440}$ | $c_{441}$ | $c_{442}$ | $c_{443}$ | $c_{444}$ | $c_{445}$ | $c_{446}$ | $c_{447}$ | $c_{448}$ | $c_{449}$ | $c_{450}$ | $c_{451}$ | $c_{452}$ | $c_{453}$ | $c_{454}$ | $c_{455}$ | $c_{456}$ | $c_{457}$ | $c_{458}$ | $c_{459}$ | $c_{460}$ | $c_{461}$ | $c_{462}$ | $c_{463}$ | $c_{464}$ | $c_{465}$ | $c_{466}$ | $c_{467}$ | $c_{468}$ | $c_{469}$ | $c_{470}$ | $c_{471}$ | $c_{472}$ | $c_{473}$ | $c_{474}$ | $c_{475}$ | $c_{476}$ | $c_{477}$ | $c_{478}$ | $c_{479}$ | $c_{480}$ | $c_{481}$ | $c_{482}$ | $c_{483}$ | $c_{484}$ | $c_{485}$ | $c_{486}$ | $c_{487}$ | $c_{488}$ | $c_{489}$ | $c_{490}$ | $c_{491}$ | $c_{492}$ | $c_{493}$ | $c_{494}$ | $c_{495}$ | $c_{496}$ | $c_{497}$ | $c_{498}$ | $c_{499}$ | $c_{500}$ | $c_{501}$ | $c_{502}$ | $c_{503}$ | $c_{504}$ | $c_{505}$ | $c_{506}$ | $c_{507}$ | $c_{508}$ | $c_{509}$ | $c_{510}$ | $c_{511}$ | $c_{512}$ | $c_{513}$ | $c_{514}$ | $c_{515}$ | $c_{516}$ | $c_{517}$ | $c_{518}$ | $c_{519}$ | $c_{520}$ | $c_{521}$ | $c_{522}$ | $c_{523}$ | $c_{524}$ | $c_{525}$ | $c_{526}$ | $c_{527}$ | $c_{528}$ | $c_{529}$ | $c_{530}$ | $c_{531}$ | $c_{532}$ | $c_{533}$ | $c_{534}$ | $c_{535}$ | $c_{536}$ | $c_{537}$ | $c_{538}$ | $c_{539}$ | $c_{540}$ | $c_{541}$ | $c_{542}$ | $c_{543}$ | $c_{544}$ | $c_{545}$ | $c_{546}$ | $c_{547}$ | $c_{548}$ | $c_{549}$ | $c_{550}$ | $c_{551}$ | $c_{552}$ | $c_{553}$ | $c_{554}$ | $c_{555}$ | $c_{556}$ | $c_{557}$ | $c_{558}$ | $c_{559}$ | $c_{560}$ | $c_{561}$ | $c_{562}$ | $c_{563}$ | $c_{564}$ | $c_{565}$ | $c_{566}$ | $c_{567}$ | $c_{568}$ | $c_{569}$ | $c_{570}$ | $c_{571}$ | $c_{572}$ | $c_{573}$ | $c_{574}$ | $c_{575}$ | $c_{576}$ | $c_{577}$ | $c_{578}$ | $c_{579}$ | $c_{580}$ | $c_{581}$ | $c_{582}$ | $c_{583}$ | $c_{584}$ | $c_{585}$ | $c_{586}$ | $c_{587}$ | $c_{588}$ | $c_{589}$ | $c_{590}$ | $c_{591}$ | $c_{592}$ | $c_{593}$ | $c_{594}$ | $c_{595}$ | $c_{596}$ | $c_{597}$ | $c_{598}$ | $c_{599}$ | $c_{600}$ | $c_{601}$ | $c_{602}$ | $c_{603}$ | $c_{604}$ | $c_{605}$ | $c_{606}$ | $c_{607}$ | $c_{608}$ | $c_{609}$ | $c_{610}$ | $c_{611}$ | $c_{612}$ | $c_{613}$ | $c_{614}$ | $c_{615}$ | $c_{616}$ | $c_{617}$ | $c_{618}$ | $c_{619}$ | $c_{620}$ | $c_{621}$ | $c_{622}$ | $c_{623}$ | $c_{624}$ | $c_{625}$ | $c_{626}$ | $c_{627}$ | $c_{628}$ | $c_{629}$ | $c_{630}$ | $c_{631}$ | $c_{632}$ | $c_{633}$ | $c_{634}$ | $c_{635}$ | $c_{636}$ | $c_{637}$ | $c_{638}$ | $c_{639}$ | $c_{640}$ | $c_{641}$ | $c_{642}$ | $c_{643}$ | $c_{644}$ | $c_{645}$ | $c_{646}$ | $c_{647}$ | $c_{648}$ | $c_{649}$ | $c_{650}$ | $c_{651}$ | $c_{652}$ | $c_{653}$ | $c_{654}$ | $c_{655}$ | $c_{656}$ | $c_{657}$ | $c_{658}$ | $c_{659}$ | $c_{660}$ | $c_{661}$ | $c_{662}$ | $c_{663}$ | $c_{664}$ | $c_{665}$ | $c_{666}$ | $c_{667}$ | $c_{668}$ | $c_{669}$ | $c_{670}$ | $c_{671}$ | $c_{672}$ | $c_{673}$ | $c_{674}$ | $c_{675}$ | $c_{676}$ | $c_{677}$ | $c_{678}$ | $c_{679}$ | $c_{680}$ | $c_{681}$ | $c_{682}$ | $c_{683}$ | $c_{684}$ | $c_{685}$ | $c_{686}$ | $c_{687}$ | $c_{688}$ | $c_{689}$ | $c_{690}$ | $c_{691}$ | $c_{692}$ | $c_{693}$ | $c_{694}$ | $c_{695}$ | $c_{696}$ | $c_{697}$ | $c_{698}$ | $c_{699}$ | $c_{700}$ | $c_{701}$ | $c_{702}$ | $c_{703}$ | $c_{704}$ | $c_{705}$ | $c_{706}$ | $c_{707}$ | $c_{708}$ | $c_{709}$ | $c_{710}$ | $c_{711}$ | $c_{712}$ | $c_{713}$ | $c_{714}$ | $c_{715}$ | $c_{716}$ | $c_{717}$ | $c_{718}$ | $c_{719}$ | $c_{720}$ | $c_{721}$ | $c_{722}$ | $c_{723}$ | $c_{724}$ | $c_{725}$ | $c_{726}$ | $c_{727}$ | $c_{728}$ | $c_{729}$ | $c_{730}$ | $c_{731}$ | $c_{732}$ | $c_{733}$ | $c_{734}$ | $c_{735}$ | $c_{736}$ | $c_{737}$ | $c_{738}$ | $c_{739}$ | $c_{740}$ | $c_{741}$ | $c_{742}$ | $c_{743}$ | $c_{744}$ | $c_{745}$ | $c_{746}$ | $c_{747}$ | $c_{748}$ | $c_{749}$ | $c_{750}$ | $c_{751}$ | $c_{752}$ | $c_{753}$ | $c_{754}$ | $c_{755}$ | $c_{756}$ | $c_{757}$ | $c_{758}$ | $c_{759}$ | $c_{760}$ | $c_{761}$ | $c_{762}$ | $c_{763}$ | $c_{764}$ | $c_{765}$ | $c_{766}$ | $c_{767}$ | $c_{768}$ | $c_{769}$ | $c_{770}$ | $c_{771}$ | $c_{772}$ | $c_{773}$ | $c_{774}$ | $c_{775}$ | $c_{776}$ | $c_{777}$ | $c_{778}$ | $c_{779}$ | $c_{780}$ | $c_{781}$ | $c_{782}$ | $c_{783}$ | $c_{784}$ | $c_{785}$ | $c_{786}$ | $c_{787}$ | $c_{788}$ | $c_{789}$ | $c_{790}$ | $c_{791}$ | $c_{792}$ | $c_{793}$ | $c_{794}$ | $c_{795}$ | $c_{796}$ | $c_{797}$ | $c_{798}$ | $c_{799}$ | $c_{800}$ | $c_{801}$ | $c_{802}$ | $c_{803}$ | $c_{804}$ | $c_{805}$ | $c_{806}$ | $c_{807}$ | $c_{808}$ | $c_{809}$ | $c_{810}$ | $c_{811}$ | $c_{812}$ | $c_{813}$ | $c_{814}$ | $c_{815}$ | $c_{816}$ | $c_{817}$ | $c_{818}$ | $c_{819}$ | $c_{820}$ | $c_{821}$ | $c_{822}$ | $c_{823}$ | $c_{824}$ | $c_{825}$ | $c_{826}$ | $c_{827}$ | $c_{828}$ | $c_{829}$ | $c_{830}$ | $c_{831}$ | $c_{832}$ | $c_{833}$ | $c_{834}$ | $c_{835}$ | $c_{836}$ | $c_{837}$ | $c_{838}$ | $c_{839}$ | $c_{840}$ | $c_{841}$ | $c_{842}$ | $c_{843}$ | $c_{844}$ | $c_{845}$ | $c_{846}$ | $c_{847}$ | $c_{848}$ | $c_{849}$ | $c_{850}$ | $c_{851}$ | $c_{852}$ | $c_{853}$ | $c_{854}$ | $c_{855}$ | $c_{856}$ | $c_{857}$ | $c_{858}$ | $c_{859}$ | $c_{860}$ | $c_{861}$ | $c_{862}$ | $c_{863}$ | $c_{864}$ | $c_{865}$ | $c_{866}$ | $c_{867}$ | $c_{868}$ | $c_{869}$ | $c_{870}$ | $c_{871}$ | $c_{872}$ | $c_{873}$ | $c_{874}$ | $c_{875}$ | $c_{876}$ | $c_{877}$ | $c_{878}$ | $c_{879}$ | $c_{880}$ | $c_{881}$ | $c_{882}$ | $c_{883}$ | $c_{884}$ | $c_{885}$ | $c_{886}$ | $c_{887}$ | $c_{888}$ | $c_{889}$ | $c_{890}$ | $c_{891}$ | $c_{892}$ | $c_{893}$ | $c_{894}$ | $c_{895}$ | $c_{896}$ | $c_{897}$ | $c_{898}$ | $c_{899}$ | $c_{900}$ | $c_{901}$ | $c_{902}$ | $c_{903}$ | $c_{904}$ | $c_{905}$ | $c_{906}$ | $c_{907}$ | $c_{908}$ | $c_{909}$ | $c_{910}$ | $c_{911}$ | $c_{912}$ | $c_{913}$ | $c_{914}$ | $c_{915}$ | $c_{916}$ | $c_{917}$ | $c_{918}$ | $c_{919}$ | $c_{920}$ | $c_{921}$ | $c_{922}$ | $c_{923}$ | $c_{924}$ | $c_{925}$ | $c_{926}$ | $c_{927}$ | $c_{928}$ | $c_{929}$ | $c_{930}$ | $c_{931}$ | $c_{932}$ | $c_{933}$ | $c_{934}$ | $c_{935}$ | $c_{936}$ | $c_{937}$ | $c_{938}$ | $c_{939}$ | $c_{940}$ | $c_{941}$ | $c_{942}$ | $c_{943}$ | $c_{944}$ | $c_{945}$ | $c_{946}$ | $c_{947}$ </ |
|----------------|-------------------------|-------------------------|---------------------------------|----------------------------------------|-------------------------------------------------|----------------------------------------|-------------------------------------------------|--------------|--------------|-------|-------|-------|-------|-------|-------|-------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|--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SULFIDES ( $C_nH_{2n+2}S_m$ ,  $n = 2, 3, 4, 5, \dots, \infty$ )

The alkyl sulfides,  $C_nH_{2n+2}S_m$ , comprise two types of  $C-S$  functional groups, one for t-butyl groups corresponding to the  $C$  and the other for the remaining general alkyl groups including methyl. The alkyl portion of the alkyl sulfide may comprise at least two terminal  
 5 methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl  
 10 ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in sulfides are equivalent to those in branched-chain alkanes.

Each  $C-S$  group is solved by hybridizing the  $2s$  and  $2p$  AOs of the  $C$  atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO  
 15 and the  $S$  AO to form a MO permits each participating orbital to decrease in radius and energy. Since the energy of sulfur is less than the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243),  $c_2$  in Eq. (15.52) is one, and the energy matching condition is determined by the  $C_2$  parameter. As in the case of thiols,  $C_2$  of Eq. (15.52) for the  $C-S$ -bond MO given by Eq. (15.127) is  $C_2(C2sp^3HO \text{ to } S) = 0.64965$ .

20 The  $C-S$  group of alkyl sulfides is equivalent to that of thiols where  $E_r(atom-atom, msp^3.AO)$  is  $-0.72457 \text{ eV}$  (Eq. (14.151)). The t-butyl- $C-S$  group is also equivalent to that of thiols except that the energy parameters corresponding to the oscillation in the transition state are matched to those of the t-butyl group.

The symbols of the functional groups of branched-chain alkyl sulfides are given in Table  
 25 15.153. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfides are given in Tables 15.154, 15.155, and 15.156, respectively. Consider that the  $C-S$  bond is along the  $x$  axis in the  $xy$ -plane. The  $S$  nucleus is at the focus  $+c$  and the  $C$  nucleus is at the focus  $-c$ . The elliptic angle  $\theta'$  is taken as counterclockwise from the  $x$ -axis for  $S$  and as clockwise from the  $-x$ -axis  
 30 for  $C$ . The total energy of each alkyl sulfide given in Table 15.157 was calculated as the sum

over the integer multiple of each  $E_D(\text{Group})$  of Table 15.156 corresponding to functional-group composition of the molecule.  $E_{mag}$  given by Eq. (15.58) was subtracted for each t-butyl group. The bond angle parameters of alkyl sulfides determined using Eqs. (15.79-15.108) are given in Table 15.158.

Table 15.153. The symbols of functional groups of alkyl sulfides.

| Functional Group               | Group Symbol           |
|--------------------------------|------------------------|
| C-S (methyl, alkyl)            | C-S (f)                |
| C-S ((CH <sub>3</sub> ), C-S-) | C-S (fi)               |
| CH <sub>3</sub> group          | C-H (CH <sub>3</sub> ) |
| CH <sub>2</sub> group          | C-H (CH <sub>2</sub> ) |
| CH                             | C-H                    |
| CC bond (n-C)                  | C-C' (a)               |
| CC bond (iso-C)                | C-C' (b)               |
| CC bond (tert-C)               | C-C' (c)               |
| CC (iso to iso-C)              | C-C' (d)               |
| CC (t to t-C)                  | C-C' (e)               |
| CC (t to iso-C)                | C-C' (f)               |

Table 15.154. The geometrical bond parameters of alkyl sulfides and experimental values [1].

| Parameter                | C-S (f)<br>Group                   | C-S (fi)<br>Group                  | C-H (CH <sub>3</sub> )<br>Group | C-H (CH <sub>2</sub> )<br>Group | C-H<br>Group      | C-C' (a)<br>Group | C-C' (b)<br>Group | C-C' (c)<br>Group | C-C' (d)<br>Group | C-C' (e)<br>Group | C-C' (f)<br>Group |
|--------------------------|------------------------------------|------------------------------------|---------------------------------|---------------------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| <i>a</i> (Å)             | 1.90975                            | 1.90975                            | 1.04920                         | 1.07122                         | 1.07465           | 2.12499           | 2.12499           | 2.10725           | 2.12499           | 2.10725           | 2.10725           |
| <i>c'</i> (Å)            | 1.71455                            | 1.71455                            | 1.04856                         | 1.05553                         | 1.05661           | 1.45744           | 1.45744           | 1.45164           | 1.45744           | 1.45164           | 1.45164           |
| Bond Length              | 1.81460                            | 1.81460                            | 1.10974                         | 1.11713                         | 1.11827           | 1.54280           | 1.54280           | 1.53635           | 1.54280           | 1.53635           | 1.53635           |
| 2 <i>c'</i> (Å)          |                                    |                                    |                                 |                                 |                   |                   |                   |                   |                   |                   |                   |
| Exp. Bond Length (Å)     | 1.807 (dimethyl sulfide)           | 1.807 (dimethyl sulfide)           | 1.107 (C-H propane)             | 1.107 (C-H propane)             | 1.122 (isobutane) | 1.532 (propane)   | 1.532 (propane)   | 1.532 (propane)   | 1.532 (propane)   | 1.532 (propane)   | 1.532 (propane)   |
|                          | 1.813 (ethyl methyl sulfide, avg.) | 1.813 (ethyl methyl sulfide, avg.) | 1.117 (C-H butane)              | 1.117 (C-H butane)              |                   | 1.531 (butane)    | 1.531 (butane)    | 1.531 (butane)    | 1.531 (butane)    | 1.531 (butane)    | 1.531 (butane)    |
| <i>t<sub>c</sub></i> (Å) | 0.84112                            | 0.84112                            | 1.27295                         | 1.29569                         | 1.29924           | 1.54616           | 1.54616           | 1.52750           | 1.54616           | 1.52750           | 1.52750           |
| <i>ε</i>                 | 0.89778                            | 0.89778                            | 0.63380                         | 0.63159                         | 0.63095           | 0.68600           | 0.68600           | 0.68888           | 0.68600           | 0.68888           | 0.68888           |

Table 15.155. The MO to HO intercept geometrical bond parameters of alkyl sulfides.  $R, R', R''$  are H or alkyl groups.  $E_f$  is  $E_f(\text{atom} - \text{atom}, \text{msp}, \text{AO})$ .

| Bond                                          | Atom | $E_f$<br>(eV)<br>Bond 1 | $E_f$<br>(eV)<br>Bond 2 | $E_f$<br>(eV)<br>Bond 3 | $E_f$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>$C2sp^3$<br>(eV) | $r_{\text{bond}}$<br>( $a_0$ ) | $r_{\text{bond}}$<br>( $a_0$ ) | $E_{\text{bond}}$<br>(eV)<br>Final | $E(C2sp^3)$<br>(eV)<br>Final | $\theta'$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | $d_1$<br>( $a_0$ ) | $d_2$<br>( $a_0$ ) |
|-----------------------------------------------|------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------------------------|--------------------------------|--------------------------------|------------------------------------|------------------------------|---------------------------|----------------------------|----------------------------|--------------------|--------------------|
| $R-S-R$<br>( $C-S$ (i) and (ii))              | S    | -0.36229                | -0.36229                | 0                       | 0                       |                                           | 1.32010                        | 0.87495                        | -15.55033                          |                              | 129.96                    | 50.04                      | 52.88                      | 1.15262            | 0.56193            |
| $H_3C-S-C_6H_5CH_2R$<br>( $C-S$ (i))          | C    | -0.36229                | 0                       | 0                       | 0                       | -151.97798                                | 0.91771                        | 0.89382                        | -15.18804                          | -14.99117                    | 130.79                    | 49.21                      | 53.75                      | 1.10937            | 0.58518            |
| $H_3C-S-C_6H_5CH_2R$<br>( $C-S$ (ii))         | C    | -0.36229                | -0.92918                | 0                       | 0                       | -152.90716                                | 0.91771                        | 0.84418                        | -16.11722                          | -15.92636                    | 128.69                    | 51.31                      | 51.57                      | 1.18689            | 0.52765            |
| $H_3C-S-C_6H_5CH_2R$<br>( $C-S$ (i) and (ii)) | C    | -0.36229                | -0.72457                | -0.72457                | -0.72457                | -154.15170                                | 0.91771                        | 0.78367                        | -17.36176                          | -17.17090                    | 125.97                    | 54.03                      | 48.94                      | 1.25430            | 0.46025            |
| $C-H$ ( $CH_3$ )                              | C    | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                | 0.91771                        | 0.86359                        | -15.75493                          | -15.56407                    | 77.49                     | 102.51                     | 41.48                      | 1.23564            | 0.18708            |
| $C-H$ ( $CH_2$ )                              | C    | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                | 0.91771                        | 0.81549                        | -16.68412                          | -16.49325                    | 68.47                     | 111.53                     | 35.84                      | 1.35486            | 0.29933            |
| $C-H$ ( $CH$ )                                | C    | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                | 0.91771                        | 0.77247                        | -17.61530                          | -17.42244                    | 61.10                     | 118.90                     | 31.37                      | 1.42988            | 0.37326            |
| $H_3C-S-C_6H_5CH_2-$<br>( $C-C$ (a))          | C    | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                | 0.91771                        | 0.86359                        | -15.75493                          | -15.56407                    | 63.82                     | 116.18                     | 30.08                      | 1.83879            | 0.38106            |
| $H_3C-S-C_6H_5CH_2-$<br>( $C-C$ (b))          | C    | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                | 0.91771                        | 0.81549                        | -16.68412                          | -16.49325                    | 56.41                     | 123.59                     | 26.06                      | 1.90890            | 0.45117            |
| $R-H_3C-S-C_6H_5CH_2-$<br>( $C-C$ (c))        | C    | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                | 0.91771                        | 0.77247                        | -17.61530                          | -17.42244                    | 48.30                     | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| $R-H_3C-S-C_6H_5CH_2-$<br>( $C-C$ (d))        | C    | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -154.71860                                | 0.91771                        | 0.75889                        | -17.92866                          | -17.73779                    | 48.21                     | 131.79                     | 21.74                      | 1.95734            | 0.50370            |
| $R-H_3C-S-C_6H_5CH_2-$<br>( $C-C$ (e))        | C    | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                | 0.91771                        | 0.77247                        | -17.61530                          | -17.42244                    | 48.30                     | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| $R-H_3C-S-C_6H_5CH_2-$<br>( $C-C$ (f))        | C    | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.51399                                | 0.91771                        | 0.76765                        | -17.92866                          | -17.73779                    | 50.04                     | 129.96                     | 22.66                      | 1.94462            | 0.49298            |
| $R-H_3C-S-C_6H_5CH_2-$<br>( $C-C$ (g))        | C    | -0.72457                | -0.92918                | -0.92918                | 0                       | -154.19863                                | 0.91771                        | 0.78155                        | -17.40869                          | -17.21783                    | 52.78                     | 127.22                     | 24.04                      | 1.92445            | 0.47279            |
| $R-H_3C-S-C_6H_5CH_2-$<br>( $C-C$ (h))        | C    | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.51399                                | 0.91771                        | 0.76765                        | -17.92866                          | -17.73779                    | 50.04                     | 129.96                     | 22.66                      | 1.94462            | 0.49298            |

Table 15.156. The energy parameters (eV) of functional groups of alkyl sulfides.

| Parameters              | C-S (i)<br>Group | C-S (ii)<br>Group | CH <sub>3</sub><br>Group | CH <sub>2</sub><br>Group | C-H<br>Group | C-C (a)<br>Group | C-C (b)<br>Group | C-C (c)<br>Group | C-C (d)<br>Group | C-C (e)<br>Group | C-C (f)<br>Group |
|-------------------------|------------------|-------------------|--------------------------|--------------------------|--------------|------------------|------------------|------------------|------------------|------------------|------------------|
| $\eta_1$                | 1                | 1                 | 3                        | 2                        | 1            | 1                | 1                | 1                | 1                | 1                | 1                |
| $\eta_2$                | 0                | 0                 | 2                        | 1                        | 0            | 0                | 0                | 0                | 0                | 0                | 0                |
| $\eta_3$                | 0                | 0                 | 0                        | 0                        | 0            | 0                | 0                | 0                | 0                | 0                | 0                |
| $\zeta_1$               | 0.5              | 0.5               | 0.75                     | 0.75                     | 0.75         | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              |
| $\zeta_2$               | 0.64965          | 0.64965           | 1                        | 1                        | 1            | 1                | 1                | 1                | 1                | 1                | 1                |
| $\zeta_3$               | 1                | 1                 | 1                        | 1                        | 1            | 1                | 1                | 1                | 1                | 1                | 1                |
| $\zeta_4$               | 1                | 1                 | 0.91771                  | 0.91771                  | 0.91771      | 0.91771          | 0.91771          | 0.91771          | 0.91771          | 0.91771          | 0.91771          |
| $\zeta_5$               | 0                | 0                 | 0                        | 1                        | 1            | 0                | 0                | 0                | 1                | 1                | 0                |
| $\zeta_6$               | 2                | 2                 | 1                        | 1                        | 1            | 2                | 2                | 2                | 2                | 2                | 2                |
| $\zeta_7$               | 0                | 0                 | 3                        | 2                        | 1            | 0                | 0                | 0                | 0                | 0                | 0                |
| $\zeta_8$               | 0.5              | 0.5               | 0.75                     | 0.75                     | 0.75         | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              |
| $\zeta_9$               | 0.64965          | 0.64965           | 1                        | 1                        | 1            | 1                | 1                | 1                | 1                | 1                | 1                |
| $\zeta_{10}$            | -46.36495        | -46.36495         | -107.32728               | -70.41425                | -35.12015    | -28.79214        | -28.79214        | -29.10112        | -28.79214        | -29.10112        | -29.10112        |
| $\zeta_{11}$            | 7.93551          | 7.93551           | 38.92728                 | 25.78002                 | 12.87680     | 9.33352          | 9.33352          | 9.37273          | 9.33352          | 9.37273          | 9.37273          |
| $\zeta_{12}$            | 12.13899         | 12.13899          | 32.53914                 | 21.06675                 | 10.48582     | 6.77464          | 6.77464          | 6.90500          | 6.77464          | 6.90500          | 6.90500          |
| $\zeta_{13}$            | -6.06949         | -6.06949          | -16.26937                | -10.53337                | -5.24291     | -3.38732         | -3.38732         | -3.45250         | -3.38732         | -3.45250         | -3.45250         |
| $\zeta_{14}$            | 0                | 0                 | -15.56407                | -15.56407                | -14.63489    | -15.56407        | -15.56407        | -15.56407        | -15.56407        | -15.56407        | -15.56407        |
| $\Delta E_{H_{10}}(eV)$ | -0.72457         | -0.72457          | 0                        | 0                        | 0            | 0                | 0                | 0                | 0                | 0                | 0                |
| $E_1(eV)$               | 0.72457          | 0.72457           | -15.56407                | -15.56407                | -14.63489    | -15.56407        | -15.56407        | -15.56407        | -15.56407        | -15.56407        | -15.56407        |
| $E_2(eV)$               | -31.63537        | -31.63537         | -67.69451                | -49.66493                | -31.63533    | -31.63537        | -31.63537        | -31.63533        | -31.63537        | -31.63533        | -31.63533        |
| $E_3(eV)$               | -0.72457         | -0.72457          | 0                        | 0                        | 0            | -1.85836         | -1.85836         | -1.44915         | -1.85836         | -1.44915         | -1.44915         |
| $E_4(eV)$               | -32.35994        | -32.35994         | -67.69450                | -49.66493                | -31.63537    | -33.49373        | -33.49373        | -33.08452        | -33.49373        | -33.08452        | -33.08452        |
| $\omega(10^{15} rad/s)$ | 30.5436          | 8.92777           | 24.9286                  | 24.2751                  | 24.1759      | 9.43699          | 9.43699          | 15.4846          | 9.43699          | 15.4846          | 9.55643          |
| $E_5(eV)$               | 20.10434         | 5.87641           | 16.40846                 | 15.97831                 | 15.91299     | 6.21159          | 6.21159          | 10.19220         | 6.21159          | 6.29021          | 6.29021          |
| $E_6(eV)$               | -0.28705         | -0.15519          | -0.25352                 | -0.25017                 | -0.24966     | -0.16515         | -0.16515         | -0.20896         | -0.16515         | -0.16416         | -0.16416         |
| $E_{K_{10}}(eV)$        | 0.08146          | 0.08146           | 0.35532                  | 0.35532                  | 0.35532      | 0.12312          | 0.17978          | 0.09944          | 0.12312          | 0.12312          | 0.12312          |
| $E_{K_{11}}(eV)$        | -0.24632         | -0.11446          | -0.22757                 | -0.14502                 | -0.07200     | -0.10359         | -0.07526         | -0.15924         | -0.10359         | -0.10260         | -0.10260         |
| $E_{K_{12}}(eV)$        | 0.14803          | 0.14803           | 0.14803                  | 0.14803                  | 0.14803      | 0.14803          | 0.14803          | 0.14803          | 0.14803          | 0.14803          | 0.14803          |
| $E_{K_{13}}(eV)$        | -32.60626        | -32.47440         | -67.92207                | -49.80996                | -31.70737    | -33.59732        | -33.49373        | -33.24376        | -33.59732        | -33.18712        | -33.18712        |
| $E_{K_{14}}(eV)$        | -14.63489        | -14.63489         | -14.63489                | -14.63489                | -14.63489    | -14.63489        | -14.63489        | -14.63489        | -14.63489        | -14.63489        | -14.63489        |
| $E_{K_{15}}(eV)$        | 0                | 0                 | -13.59844                | -13.59844                | -13.59844    | 0                | 0                | 0                | 0                | 0                | 0                |
| $E_{K_{16}}(eV)$        | 3.33648          | 3.20462           | 12.49186                 | 7.83016                  | 3.32601      | 4.32754          | 4.29921          | 3.97398          | 4.17951          | 3.62128          | 3.91734          |

Table 15.157. The total bond energies of alkyl sulfides calculated using the functional group composition and the energies of Table 15.156 compared to the experimental values [3]. The magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_{D(mag)} (eV)$  values based on composition is given by (15.58).

| Formula                          | Name                     | C-S (i)<br>Group | C-S (ii)<br>Group | CH <sub>3</sub> | CH <sub>2</sub> | CH | C-C (a) | C-C (b) | C-C (c) | C-C (d) | C-C (e) | C-C (f) | $E_{mag}$ | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|----------------------------------|--------------------------|------------------|-------------------|-----------------|-----------------|----|---------|---------|---------|---------|---------|---------|-----------|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>2</sub> H <sub>6</sub> S  | Dimethyl sulfide         | 2                | 0                 | 2               | 0               | 0  | 0       | 0       | 0       | 0       | 0       | 0       | 0         | 31.6568                                 | 31.672                                    | 0.00048        |
| C <sub>3</sub> H <sub>8</sub> S  | Ethyl methyl sulfide     | 1                | 0                 | 2               | 1               | 0  | 0       | 0       | 0       | 0       | 0       | 0       | 0         | 43.8138                                 | 43.848                                    | 0.00078        |
| C <sub>4</sub> H <sub>10</sub> S | Diethyl sulfide          | 2                | 0                 | 2               | 2               | 0  | 0       | 0       | 0       | 0       | 0       | 0       | 0         | 55.97208                                | 56.043                                    | 0.00126        |
| C <sub>5</sub> H <sub>12</sub> S | Methyl propyl sulfide    | 2                | 0                 | 2               | 2               | 0  | 0       | 0       | 0       | 0       | 0       | 0       | 0         | 55.97208                                | 56.029                                    | 0.00102        |
| C <sub>6</sub> H <sub>14</sub> S | Isopropyl methyl sulfide | 2                | 0                 | 3               | 0               | 1  | 0       | 2       | 0       | 0       | 0       | 0       | 0         | 56.07297                                | 56.115                                    | 0.00075        |
| C <sub>6</sub> H <sub>14</sub> S | Butyl methyl sulfide     | 2                | 0                 | 2               | 3               | 0  | 3       | 0       | 0       | 0       | 0       | 0       | 0         | 68.12978                                | 68.185                                    | 0.00081        |
| C <sub>6</sub> H <sub>14</sub> S | t-Butyl methyl sulfide   | 1                | 1                 | 4               | 0               | 0  | 0       | 0       | 3       | 0       | 0       | 0       | -1        | 68.28245                                | 68.381                                    | 0.00144        |
| C <sub>6</sub> H <sub>14</sub> S | Ethyl propyl sulfide     | 1                | 0                 | 2               | 3               | 0  | 3       | 0       | 0       | 0       | 0       | 0       | 0         | 68.12978                                | 68.210                                    | 0.00117        |
| C <sub>6</sub> H <sub>14</sub> S | Diisopropyl sulfide      | 2                | 0                 | 3               | 2               | 1  | 1       | 0       | 0       | 0       | 0       | 0       | 0         | 68.23067                                | 68.350                                    | 0.00174        |
| C <sub>6</sub> H <sub>14</sub> S | Butyl ethyl sulfide      | 2                | 0                 | 2               | 4               | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0         | 80.48926                                | 80.542                                    | 0.00065        |
| C <sub>6</sub> H <sub>14</sub> S | Methyl pentyl sulfide    | 2                | 0                 | 2               | 4               | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0         | 80.28748                                | 80.395                                    | 0.00133        |
| C <sub>6</sub> H <sub>14</sub> S | Diethyl sulfide          | 2                | 0                 | 2               | 6               | 0  | 6       | 0       | 0       | 0       | 0       | 0       | 0         | 80.28748                                | 80.332                                    | 0.00056        |
| C <sub>6</sub> H <sub>14</sub> S | Di-sec-butyl sulfide     | 2                | 0                 | 2               | 4               | 2  | 2       | 4       | 0       | 0       | 0       | 0       | 0         | 104.60288                               | 104.701                                   | 0.00094        |
| C <sub>6</sub> H <sub>14</sub> S | Di-t-butyl sulfide       | 0                | 2                 | 6               | 0               | 0  | 0       | 0       | 6       | 0       | 0       | 0       | 0         | 104.80466                               | 104.701                                   | -0.00099       |
| C <sub>6</sub> H <sub>14</sub> S | Dipentyl sulfide         | 2                | 0                 | 4               | 2               | 2  | 0       | 0       | 0       | 0       | 0       | 0       | -2        | 104.90822                               | 104.920                                   | 0.00011        |
| C <sub>6</sub> H <sub>14</sub> S | Diisobutyl sulfide       | 2                | 0                 | 4               | 2               | 0  | 0       | 6       | 0       | 0       | 0       | 0       | 0         | 104.74800                               | 104.834                                   | 0.00082        |
| C <sub>6</sub> H <sub>14</sub> S | Dipentyl sulfide         | 2                | 0                 | 2               | 8               | 0  | 8       | 0       | 0       | 0       | 0       | 0       | 0         | 128.91828                               | 128.979                                   | 0.00047        |
| C <sub>6</sub> H <sub>14</sub> S | Diisopentyl sulfide      | 2                | 0                 | 4               | 4               | 2  | 2       | 6       | 0       | 0       | 0       | 0       | 0         | 129.06340                               | 129.151                                   | 0.00068        |



# DISULFIDES ( $C_nH_{2n+2}S_{2m}$ , $n = 2, 3, 4, 5, \dots, \infty$ )

The alkyl disulfides,  $C_nH_{2n+2}S_{2m}$ , comprise  $C-S$  and  $S-S$  functional groups. The alkyl portion of the alkyl disulfide may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in disulfides are equivalent to those in branched-chain alkanes.

Each  $C-S$  group is equivalent to that of general alkyl sulfides given in the corresponding section. As in the case of thiols and sulfides,  $C_2$  of Eq. (15.52) for the  $C-S$  bond MO given by Eq. (15.127) is  $C_2(C2sp^3HO \text{ to } S) = 0.64965$  and  $E_T(atom - atom, msp^3.AO)$  is  $-0.72457 \text{ eV}$  (Eq. (14.151)).

The  $S-S$  group is solved as an  $H_2$ -type-ellipsoidal-MO that is energy matched to the energy of sulfur,  $E(S) = -10.36001 \text{ eV}$ , such that  $E(AO / HO) = -10.36001 \text{ eV}$  in Eq. (15.42) with  $E_T(AO / HO) = E(AO / HO)$ . The  $S-S$ -bond MO is further energy matched to the  $C2sp^3$  HO of the  $C-S$ -bond MO.  $C_2$  of Eq. (15.52) for the  $S-S$ -bond MO given by Eq. (15.127) is also  $C_2(C2sp^3HO \text{ to } S) = 0.64965$ . In order to match  $E_T(atom - atom, msp^3.AO)$  of the  $C-S$  group ( $-0.72457 \text{ eV}$  (Eq. (14.151))),  $E_T(atom - atom, msp^3.AO)$  of the  $S-S$ -bond MO is determined using a linear combination of the AOs corresponding to  $-0.72457 \text{ eV}$  and  $0 \text{ eV}$  in Eq. (15.29), Eq. (15.31), and Eqs. (15.19-15.20). The result corresponding to bond order 1/2I in Table 15.2 is  $E_T(atom - atom, msp^3.AO) = -0.36229 \text{ eV}$ .

The symbols of the functional groups of branched-chain alkyl disulfides are given in Table 15.159. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl disulfides are given in Tables 15.160, 15.161, and 15.162, respectively. The total energy of each alkyl disulfide given



in Table 15.163 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.162 corresponding to functional-group composition of the molecule.  $E_{mag}$  given by Eq. (15.58) was subtracted for each t-butyl group. The bond angle parameters of alkyl disulfides determined using Eqs. (15.79-15.108) are given in Table 15.164.

Table 15.159. The symbols of functional groups of alkyl disulfides.

| Functional Group      | Group Symbol           |
|-----------------------|------------------------|
| C-S                   | C-S                    |
| S-S                   | S-S                    |
| CH <sub>3</sub> group | C-H (CH <sub>3</sub> ) |
| CH <sub>2</sub> group | C-H (CH <sub>2</sub> ) |
| CH                    | C-H                    |
| CC bond (n-C)         | C-C (a)                |
| CC bond (iso-C)       | C-C (b)                |
| CC bond (tert-C)      | C-C (c)                |
| CC (iso to iso-C)     | C-C (d)                |
| CC (t to t-C)         | C-C (e)                |
| CC (t to iso-C)       | C-C (f)                |

Table 15.160. The geometrical bond parameters of alkyl disulfides and experimental values [1].

| Parameter                | C-S (f)<br>Group              | S-S<br>Group                  | C-H (CH <sub>3</sub> )<br>Group                 | C-H (CH <sub>2</sub> )<br>Group                 | C-H<br>Group         | C-C (a)<br>Group                        | C-C (b)<br>Group                        | C-C (c)<br>Group                        | C-C (d)<br>Group                        | C-C (e)<br>Group                        | C-C (f)<br>Group                        |
|--------------------------|-------------------------------|-------------------------------|-------------------------------------------------|-------------------------------------------------|----------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|
| $a$ (Å)                  | 1.90975                       | 2.37173                       | 1.64920                                         | 1.67122                                         | 1.67465              | 2.12499                                 | 2.12499                                 | 2.10725                                 | 2.12499                                 | 2.10725                                 | 2.10725                                 |
| $c'$ (Å)                 | 1.71455                       | 1.91070                       | 1.04856                                         | 1.05553                                         | 1.05661              | 1.45744                                 | 1.45744                                 | 1.45164                                 | 1.45744                                 | 1.45164                                 | 1.45164                                 |
| Bond Length<br>$2c'$ (Å) | 1.81460                       | 2.02220                       | 1.10974                                         | 1.11713                                         | 1.11827              | 1.54280                                 | 1.54280                                 | 1.53635                                 | 1.54280                                 | 1.53635                                 | 1.53635                                 |
| Exp. Bond Length<br>(Å)  | 1.816<br>(dimethyl disulfide) | 2.029<br>(dimethyl disulfide) | 1.107<br>(C-H propane)<br>1.117<br>(C-H butane) | 1.107<br>(C-H propane)<br>1.117<br>(C-H butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $b, c$ (Å)               | 0.84112                       | 1.40510                       | 1.27295                                         | 1.29569                                         | 1.29924              | 1.54616                                 | 1.54616                                 | 1.52750                                 | 1.54616                                 | 1.52750                                 | 1.52750                                 |
| $e$                      | 0.89778                       | 0.80562                       | 0.63580                                         | 0.63159                                         | 0.63095              | 0.68600                                 | 0.68600                                 | 0.68888                                 | 0.68600                                 | 0.68888                                 | 0.68888                                 |

Table 15.161. The MO to HO intercept geometrical bond parameters of alkyl disulfides.  $R, R', R''$  are H or alkyl groups.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{msp}, \text{AO})$ .

| Bond                                                    | Atom           | $E_T$<br>(eV)<br>Bond 1 | $E_T$<br>(eV)<br>Bond 2 | $E_T$<br>(eV)<br>Bond 3 | $E_T$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>(eV) | $r_{\text{final}}$<br>( $a_0$ ) | $E_{\text{residual}}$<br>(eV)<br>Final | $E(C2sp^2)$<br>(eV)<br>Final | $\theta'$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | $d_1$<br>( $a_0$ ) | $d_2$<br>( $a_0$ ) |
|---------------------------------------------------------|----------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------------|---------------------------------|----------------------------------------|------------------------------|---------------------------|----------------------------|----------------------------|--------------------|--------------------|
| RS-SR<br>(C-S (I) and (II))                             | S              | -0.36229                | -0.18114                | 0                       | 0                       |                               | 1.32010                         | -15.36918                              |                              | 94.25                     | 85.75                      | 38.93                      | 1.84513            | 0.06558            |
| $H_3C_a-SS-C_aH_2CH_2R$                                 | C <sub>a</sub> | -0.36229                | 0                       | 0                       | 0                       | -151.97798                    | 0.91771                         | -15.18804                              | -14.99717                    | 130.79                    | 49.21                      | 53.75                      | 1.12937            | 0.58518            |
| $H_3C_a-SS-C_aH_2CH_2R$<br>(C-S (I))                    | C <sub>a</sub> | -0.36229                | -0.92918                | 0                       | 0                       | -152.90716                    | 0.91771                         | -16.11722                              | -15.92636                    | 128.69                    | 51.31                      | 51.57                      | 1.18689            | 0.52765            |
| C-H (CH <sub>3</sub> )                                  | C <sub>e</sub> | -0.36229                | -0.72457                | -0.72457                | -0.72457                | -154.15170                    | 0.91771                         | -17.36176                              | -17.17090                    | 125.97                    | 54.03                      | 48.94                      | 1.25430            | 0.46025            |
| C-H (CH <sub>2</sub> )                                  | C <sub>i</sub> | -0.92918                | 0                       | 0                       | 0                       | -152.54487                    | 0.91771                         | -15.75493                              | -15.56407                    | 77.49                     | 102.51                     | 41.48                      | 1.25564            | 0.18708            |
| C-H (CH <sub>2</sub> )                                  | C <sub>i</sub> | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                    | 0.91771                         | -16.68412                              | -16.49325                    | 68.47                     | 111.53                     | 35.84                      | 1.35486            | 0.20933            |
| C-H (CH)                                                | C <sub>i</sub> | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40524                    | 0.91771                         | -17.61330                              | -17.42244                    | 61.10                     | 118.90                     | 31.57                      | 1.42988            | 0.37326            |
| $H_3C_aC_aH_2CH_2-$<br>(C-C (II))                       | C <sub>a</sub> | -0.92918                | 0                       | 0                       | 0                       | -152.54487                    | 0.91771                         | -15.75493                              | -15.56407                    | 63.82                     | 116.18                     | 30.08                      | 1.83879            | 0.38106            |
| $R-H_2C_a(H_2C_a-R')HCCH_2-$<br>(C-C (II))              | C <sub>a</sub> | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                    | 0.91771                         | -16.68412                              | -16.49325                    | 56.41                     | 123.59                     | 26.06                      | 1.90890            | 0.45117            |
| $R-H_2C_a(R'-H_2C_a)C_a(R''-H_2C_a)CH_2-$<br>(C-C (II)) | C <sub>a</sub> | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40524                    | 0.91771                         | -17.61330                              | -17.42244                    | 48.30                     | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| $isoC_aC_a(H_2C_a-R')HCCH_2-$<br>(C-C (II))             | C <sub>a</sub> | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -154.71860                    | 0.91771                         | -17.92866                              | -17.73779                    | 48.21                     | 131.79                     | 21.74                      | 1.97354            | 0.50570            |
| $tertC_a(R'-H_2C_a)C_a(R''-H_2C_a)CH_2-$<br>(C-C (II))  | C <sub>a</sub> | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40524                    | 0.91771                         | -17.61330                              | -17.42244                    | 48.30                     | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| $tertC_a(H_2C_a-R')HCCH_2-$<br>(C-C (II))               | C <sub>a</sub> | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.51399                    | 0.91771                         | -17.92866                              | -17.73779                    | 50.04                     | 129.56                     | 22.66                      | 1.94462            | 0.49298            |
| $tertC_a(H_2C_a-R')HCCH_2-$<br>(C-C (II))               | C <sub>a</sub> | -0.72457                | -0.92918                | -0.92918                | 0                       | -154.19863                    | 0.91771                         | -17.40869                              | -17.21783                    | 52.78                     | 127.22                     | 24.04                      | 1.92443            | 0.47279            |
| $tertC_a(R'-H_2C_a)C_a(R''-H_2C_a)CH_2-$<br>(C-C (II))  | C <sub>a</sub> | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.51399                    | 0.91771                         | -17.92866                              | -17.73779                    | 50.04                     | 129.56                     | 22.66                      | 1.94462            | 0.49298            |

Table 15.162. The energy parameters (eV) of functional groups of alkyl disulfides.

| Parameters                        | C-S (f)   | S-S Group | C-H <sub>2</sub> Group | C-H Group | C-C (a) Group | C-C (b) Group | C-C (c) Group | C-C (d) Group | C-C (e) Group | C-C (f) Group | C-C (f) Group |
|-----------------------------------|-----------|-----------|------------------------|-----------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| $\eta_1$                          | 1         | 1         | 3                      | 1         | 1             | 1             | 1             | 1             | 1             | 1             | 1             |
| $\eta_2$                          | 0         | 0         | 2                      | 0         | 0             | 0             | 0             | 0             | 0             | 0             | 0             |
| $\eta_3$                          | 0         | 0         | 0                      | 0         | 0             | 0             | 0             | 0             | 0             | 0             | 0             |
| $\zeta_1$                         | 0.5       | 0.5       | 0.75                   | 0.75      | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           |
| $\zeta_2$                         | 0.64965   | 0.64965   | 1                      | 1         | 1             | 1             | 1             | 1             | 1             | 1             | 1             |
| $\zeta_3$                         | 1         | 1         | 1                      | 1         | 1             | 1             | 1             | 1             | 1             | 1             | 1             |
| $\zeta_4$                         | 1         | 1         | 0.91771                | 0.91771   | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       |
| $\zeta_5$                         | 0         | 0         | 0                      | 1         | 0             | 0             | 0             | 1             | 1             | 1             | 0             |
| $\zeta_6$                         | 2         | 2         | 1                      | 1         | 2             | 2             | 2             | 2             | 2             | 2             | 2             |
| $\zeta_7$                         | 0         | 0         | 3                      | 1         | 0             | 0             | 0             | 0             | 0             | 0             | 0             |
| $\zeta_{10}$                      | 0.5       | 0.5       | 0.75                   | 0.75      | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           |
| $\zeta_{20}$                      | 0.64965   | 0.64965   | 1                      | 1         | 1             | 1             | 1             | 1             | 1             | 1             | 1             |
| $V_e$ (eV)                        | -46.36495 | -31.74215 | -107.32728             | -70.41425 | -28.79214     | -28.79214     | -28.79214     | -28.79214     | -29.10112     | -29.10112     | -29.10112     |
| $V_p$ (eV)                        | 7.95551   | 7.12083   | 38.92728               | 25.78002  | 9.33552       | 9.33552       | 9.33552       | 9.33552       | 9.37273       | 9.37273       | 9.37273       |
| $T$ (eV)                          | 12.13899  | 6.69177   | 32.53914               | 21.06675  | 6.77464       | 6.77464       | 6.77464       | 6.77464       | 6.90500       | 6.90500       | 6.90500       |
| $V_m$ (eV)                        | -6.06949  | -3.34589  | -16.24697              | -10.53337 | -3.38732      | -3.38732      | -3.38732      | -3.38732      | -3.45250      | -3.45250      | -3.45250      |
| $E_{1/2}^{\text{red}}(eV)$        | 0         | -10.36001 | -15.56407              | -15.56407 | -15.56407     | -15.56407     | -15.56407     | -15.56407     | -15.56407     | -15.56407     | -15.56407     |
| $\Delta F_{H_{1/2}}(eV)$          | -0.72457  | 0         | 0                      | 0         | 0             | 0             | 0             | 0             | 0             | 0             | 0             |
| $E_{1/2}^{\text{red}}(eV)$        | 0.72457   | -10.36001 | -15.56407              | -15.56407 | -15.56407     | -15.56407     | -15.56407     | -15.56407     | -15.56407     | -15.56407     | -15.56407     |
| $E_{1/2}^{\text{ox}}(eV)$         | -31.63537 | -31.63544 | -67.69451              | -49.66493 | -31.63537     | -31.63537     | -31.63537     | -31.63537     | -31.63537     | -31.63537     | -31.63537     |
| $E_{1/2}^{\text{ox}}(eV)$         | -0.72457  | -0.36229  | 0                      | 0         | -1.85836      | -1.85836      | -1.4915       | -1.4915       | -1.4915       | -1.4915       | -1.4915       |
| $E_{1/2}^{\text{ox}}(eV)$         | -32.35994 | -31.99766 | -67.69450              | -49.66493 | -33.49373     | -33.49373     | -33.49373     | -33.49373     | -33.49373     | -33.49373     | -33.49373     |
| $\omega$ (10 <sup>16</sup> rad/s) | 30.5436   | 6.45076   | 24.9286                | 24.2751   | 9.43699       | 9.43699       | 9.43699       | 9.43699       | 9.55643       | 9.55643       | 9.55643       |
| $E_k$ (eV)                        | 20.10434  | 4.24600   | 16.40846               | 15.97831  | 6.21159       | 6.21159       | 6.21159       | 6.21159       | 6.29021       | 6.29021       | 6.29021       |
| $E_p$ (eV)                        | -0.28705  | -0.13044  | -0.23552               | -0.23017  | -0.16515      | -0.16515      | -0.16515      | -0.16515      | -0.16416      | -0.16416      | -0.16416      |
| $E_{\text{red}}$ (eV)             | 0.08146   | 0.06745   | 0.35532                | 0.35532   | 0.12312       | 0.12312       | 0.12312       | 0.12312       | 0.12312       | 0.12312       | 0.12312       |
| $E_{\text{red}}$ (eV)             | -0.24652  | -0.09672  | -0.22757               | -0.14502  | -0.10359      | -0.10359      | -0.10359      | -0.10359      | -0.10260      | -0.10260      | -0.10260      |
| $E_{\text{red}}$ (eV)             | 0.14803   | 0.14803   | 0.14803                | 0.14803   | 0.14803       | 0.14803       | 0.14803       | 0.14803       | 0.14803       | 0.14803       | 0.14803       |
| $E_{1/2}^{\text{red}}$ (eV)       | -32.60626 | -32.09437 | -67.92207              | -49.80996 | -33.59732     | -33.59732     | -33.59732     | -33.59732     | -33.59732     | -33.59732     | -33.59732     |
| $E_{\text{red}}$ (eV)             | -14.63489 | -14.63489 | -14.63489              | -14.63489 | -14.63489     | -14.63489     | -14.63489     | -14.63489     | -14.63489     | -14.63489     | -14.63489     |
| $E_{\text{red}}$ (eV)             | 0         | 0         | -13.59844              | -13.59844 | 0             | 0             | 0             | 0             | 0             | 0             | 0             |
| $E_{1/2}^{\text{red}}$ (eV)       | 3.35648   | 2.82459   | 12.49186               | 7.83016   | 4.32754       | 4.29921       | 3.97398       | 4.17951       | 3.62128       | 3.62128       | 3.62128       |

Table 15.163. The total bond energies of alkyl disulfides calculated using the functional group composition and the energies of Table 15.162 compared to the experimental values [3]. The magnetic energy  $E_{\text{mag}}$  that is subtracted from the weighted sum of the  $E_{1/2}^{\text{red}}$  (eV) values based on composition is given by (15.58).

| Formula                           | Name               | C-S Group | S-S Group | C-H <sub>2</sub> | CH | C-C (a) | C-C (b) | C-C (c) | C-C (d) | C-C (e) | C-C (f) | $E_{\text{mag}}$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|-----------------------------------|--------------------|-----------|-----------|------------------|----|---------|---------|---------|---------|---------|---------|------------------|-----------------------------------|-------------------------------------|----------------|
| $\text{CH}_3\text{SS}_2$          | Dimethyl disulfide | 2         | 1         | 2                | 0  | 0       | 0       | 0       | 0       | 0       | 0       | 0                | 34.413                            | 34.413                              | -0.00199       |
| $\text{C}_2\text{H}_5\text{SS}_2$ | Ethyl disulfide    | 2         | 1         | 2                | 0  | 2       | 0       | 0       | 0       | 0       | 0       | 0                | 58.79667                          | 58.873                              | 0.00120        |
| $\text{C}_3\text{H}_7\text{SS}_2$ | Propyl disulfide   | 2         | 1         | 2                | 0  | 4       | 0       | 0       | 0       | 0       | 0       | 0                | 83.1207                           | 83.169                              | 0.00068        |
| $\text{C}_4\text{H}_9\text{SS}_2$ | Butyl disulfide    | 2         | 1         | 6                | 0  | 0       | 0       | 6       | 0       | 0       | 0       | -2               | 107.99653                         | 107.919                             | -0.00072       |



SULFOXIDES ( $C_nH_{2n+2}(SO)_m$ ,  $n = 2, 3, 4, 5 \dots \infty$ )

The alkyl sulfoxides,  $C_nH_{2n+2}(SO)_m$ , comprise a  $C-SO-C$  moiety that comprises  $C-S$  and  $SO$  functional groups. The alkyl portion of the alkyl sulfoxide may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in sulfoxides are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is  $1s^2 2s^2 2p^4$ , and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state  $^3P_2$ . The  $SO$  functional group comprises a double bond between the two unpaired electrons of  $O$ . The sulfur atom is energy matched to the  $C2sp^3$  HO. In alkyl sulfoxides, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)), and the  $S$  AO has an initial energy of  $E(S) = -10.36001 \text{ eV}$  [38]. To meet the equipotential condition of the union of the  $S=O$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the  $S=O$ -bond MO given by Eqs. (15.68) and (15.70) is

$$\begin{aligned} c_2(O \text{ to } S3sp^3 \text{ to } C2sp^3 HO) &= \frac{E(O)}{E(S)} c_2(C2sp^3 HO) \\ &= \frac{-13.61806 \text{ eV}}{-10.36001 \text{ eV}} (0.91771) \\ &= 1.20632 \end{aligned} \quad (15.128)$$

The  $S$  atom also forms a single bond with each of the  $C2sp^3$  HOs of the two  $C-S$  groups. The formation of these bonds is permitted by the hybridization of the four electrons of the  $S3p$  shell to give the orbital arrangement:

$$\begin{array}{cccc} & \text{3sp}^3 \text{ state} & & \\ \uparrow & \uparrow & \uparrow & \uparrow \\ \hline 0,0 & 1,-1 & 1,0 & 1,1 \end{array} \quad (15.129)$$

where the quantum numbers ( $\ell, m_\ell$ ) are below each electron. The  $3s$  shell remains unchanged. Then, the Coulombic energy  $E_{Coulomb}(S, 3sp^3)$  of the outer electron of the  $S3sp^3$  shell given by Eq. (15.118) with  $r_{3sp^3} = 1.17585a_0$  (Eq. (15.119)) is  $-11.57099 \text{ eV}$ . Using Eq. (15.16) with the radius of the sulfur atom  $r_{16} = 1.32010a_0$  given by Eq. (10.341), the energy  $E(S3sp^3)$  of the

5 outer electron of the  $S3sp^3$  shell is given by the sum of  $E_{Coulomb}(S3sp^3)$  and  $E(magnetic)$ :

$$\begin{aligned}
 E(S3sp^3) &= \frac{-e^2}{8\pi\epsilon_0 r_{3sp^3}} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 r_{16}^3} \\
 &= \frac{-e^2}{8\pi\epsilon_0 1.17585a_0} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 (1.32010a_0)^3} \\
 &= -11.57099 \text{ eV} + 0.04973 \\
 &= -11.52126 \text{ eV}
 \end{aligned} \tag{15.130}$$

Then, the hybridization energy  $E_{hybridization}(S3sp^3)$  of the  $S3sp^3$  HO is

$$\begin{aligned}
 E_{hybridization}(S3sp^3) &= E(S3sp^3) - E(S) \\
 &= -11.52126 \text{ eV} - 10.36001 \text{ eV} \\
 &= -1.16125 \text{ eV}
 \end{aligned} \tag{15.131}$$

The  $SO$  group is matched to the  $C-S$  group with which it shares the common

10 hybridized  $S$  atom. Consequently,  $E_{hybridization}(S3sp^3)$  is subtracted from  $E_r(Group)$  in the determination of  $E_D(Group)$  (Eq. 15.56)). Furthermore, the energy of the  $S=O$ -bond MO is the sum of the component energies of the  $H_2$ -type ellipsoidal MO given in Eq. (15.42) with the energy matched to the final energy of the hybridized  $S$  atom such that

$$E(AO / HO) = E(S3sp^3) = -11.52126 \text{ eV} \quad \text{a n d}$$

$$15 \quad \Delta E_{H_2MO}(AO / HO) = E_{hybridization}(S3sp^3) = -1.16125 \text{ eV} . \quad \text{T h e n ,}$$

$E_r(AO / HO) = E(S) = -10.36001 \text{ eV}$ . Also,  $E_r(atom - atom, msp^3.AO)$  of the  $S=O$  bond is zero since there are no bonds with a  $C2sp^3$  HO.

The  $C-S$  group is solved as an energy minimum by hybridizing the  $2s$  and  $2p$  AOs of the  $C$  atom to form a single  $2sp^3$  shell and by hybridizing the four  $S3p$  electrons to form a

20  $S3sp^3$  shell, and the sharing of electrons between the  $C2sp^3$  HO and the  $S3sp^3$  HO to form a MO permits each participating orbital to decrease in radius and energy. Using the Coulombic

energy of the  $S3sp^3$  shell,  $E_{Coulomb}(S3sp^3)$  given by Eq. (15.120) in Eq. (15.63), the  $S3sp^3$ -shell hybridization factor,  $c_2(S3sp^3)$ , is

$$c_2(S3sp^3) = \frac{E_{Coulomb}(S3sp^3)}{E(H)} = \frac{-11.57099 \text{ eV}}{-13.60580 \text{ eV}} = 0.85045 \quad (15.132)$$

As in the case of thiols, sulfides, and disulfides, the energy of sulfur is less than the  
 5 Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). Thus,  $c_1$  and  $c_2$   
 are equal to one in Eq. (15.52), and the energy matching condition is determined by the  $C_2$   
 parameter. In alkyl sulfoxides, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq.  
 (13.430)) with a corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)) and the  
 $S3sp^3$  HO has an energy of  $E(S3sp^3) = -11.52126 \text{ eV}$  (Eq. (15.130)). To meet the  
 10 equipotential condition of the union of the  $C-S$   $H_2$ -type-ellipsoidal-MO with these orbitals,  
 the hybridization factor  $C_2$  of Eq. (15.52) for the  $C-S$ -bond MO given by Eqs. (15.68) and  
 (15.70) is

$$C_2(C2sp^3HO \text{ to } S3sp^3) = \frac{E(S3sp^3)}{E(C, 2sp^3)} c_2(S3sp^3) = \frac{-11.52126 \text{ eV}}{-14.63489 \text{ eV}} (0.85045) = 0.66951 \quad (15.133)$$

As in the case of thiols, sulfides, and disulfides, with the energy of  $S$  matched to the  
 15 Coulombic energy between the electron and proton of  $H$ , the energy of the  $C-S$ -bond MO is  
 the sum of the component energies of the  $H_2$ -type ellipsoidal MO given in Eq. (15.42) with

$$E(AO/HO) = 0 \quad \text{and} \quad E_T(AO/HO) = \Delta E_{H_2MO}(AO/HO). \quad \text{For sulfoxides,}$$

$$\Delta E_{H_2MO}(AO/HO) = -0.72457 \text{ eV}. \quad \text{Further equivalently,}$$

$$E_T(atom - atom, msp^3.AO) = -0.72457 \text{ eV} \quad (\text{Eq. (14.151)}).$$

20 The symbols of the functional groups of branched-chain alkyl sulfoxides are given in  
 Table 15.165. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)),  
 and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfoxides are given in  
 Tables 15.166, 15.167, and 15.168, respectively. Consider that the  $C-S$  bond is along the  $x$   
 axis in the  $xy$ -plane. The  $S$  nucleus is at the focus  $+c$  and the  $C$  nucleus is at the focus  $-c$ . The  
 25 elliptic angle  $\theta'$  is taken as counterclockwise from the  $x$ -axis for  $S$  and as clockwise from the  
 $-x$ -axis for  $C$ . The total energy of each alkyl sulfoxide given in Table 15.169 was calculated as  
 the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.168 corresponding to functional-



group composition of the molecule. The bond angle parameters of alkyl sulfoxides determined using Eqs. (15.79-15.108) are given in Table 15.170.

Table 15.165. The symbols of functional groups of alkyl sulfoxides.

| Functional Group      | Group Symbol |
|-----------------------|--------------|
| C-S                   | $C-S$        |
| SO                    | $SO$         |
| CH <sub>3</sub> group | $C-H (CH_3)$ |
| CH <sub>2</sub> group | $C-H (CH_2)$ |
| CH                    | $C-H$        |
| CC bond (n-C)         | $C-C (a)$    |
| CC bond (iso-C)       | $C-C (b)$    |
| CC bond (tert-C)      | $C-C (c)$    |
| CC (iso to iso-C)     | $C-C (d)$    |
| CC (t to t-C)         | $C-C (e)$    |
| CC (t to iso-C)       | $C-C (f)$    |

Table 15.166. The geometrical bond parameters of alkyl sulfoxides and experimental values [1].

| Parameter            | C-S<br>Group | S-O<br>Group         | C'-H (CH <sub>3</sub> )<br>Group | C-H (CH <sub>2</sub> )<br>Group | C'-C' (a)<br>Group | C'-C' (b)<br>Group | C-C' (c)<br>Group | C-C' (d)<br>Group | C-C' (e)<br>Group | C-C' (f)<br>Group |
|----------------------|--------------|----------------------|----------------------------------|---------------------------------|--------------------|--------------------|-------------------|-------------------|-------------------|-------------------|
| $\alpha$ (a)         | 1.87325      | 1.98517              | 1.64920                          | 1.67122                         | 1.67465            | 1.67465            | 2.12499           | 2.10725           | 2.10725           | 2.10725           |
| $c'$ (a)             | 1.67271      | 1.40896              | 1.04856                          | 1.05553                         | 1.05661            | 1.05661            | 1.45744           | 1.45164           | 1.45164           | 1.45164           |
| Bond Length          |              |                      |                                  |                                 |                    |                    |                   |                   |                   |                   |
| $2c'$ (A)            | 1.77031      | 1.49118              | 1.10974                          | 1.11713                         | 1.11827            | 1.11827            | 1.54280           | 1.53635           | 1.53635           | 1.53635           |
| Exp. Bond Length     |              |                      |                                  |                                 |                    |                    |                   |                   |                   |                   |
| (dimethyl sulfoxide) | 1.799        | 1.485                | 1.107                            | 1.107                           | 1.122              | 1.122              | 1.532             | 1.532             | 1.532             | 1.532             |
| (A)                  |              | (dimethyl sulfoxide) | (C-H propane)                    | (C-H propane)                   | (isobutane)        | (isobutane)        | (butane)          | (butane)          | (butane)          | (butane)          |
| $h, c'$ (a)          | 0.84328      | 1.39847              | 1.27295                          | 1.29569                         | 1.29924            | 1.29924            | 1.54616           | 1.52750           | 1.52750           | 1.52750           |
| $\sigma$             | 0.89294      | 0.70974              | 0.63580                          | 0.63159                         | 0.63095            | 0.63095            | 0.68600           | 0.68888           | 0.68888           | 0.68888           |

Table 15.167. The MO to HO intercept geometrical bond parameters of alkyl sulfoxides.  $E_r$  is  $E_r$  (atom - atom, msp, AO).

| Bond                                      | Atom           | $E_r$ (eV)<br>Bond 1 | $E_r$ (eV)<br>Bond 2 | $E_r$ (eV)<br>Bond 3 | $E_r$ (eV)<br>Bond 4 | Final Total<br>Energy C2sp <sup>3</sup> (eV) | $r_{\text{final}}$ (a) | $r_{\text{final}}$ (a) | $E_{\text{orbital}}$ (eV)<br>Final | $E$ (C2sp <sup>3</sup> )<br>(eV)<br>Final | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ (a) | $d_2$ (a) |
|-------------------------------------------|----------------|----------------------|----------------------|----------------------|----------------------|----------------------------------------------|------------------------|------------------------|------------------------------------|-------------------------------------------|----------------|----------------|-----------|-----------|
| $R_2S=O$                                  | S              | 0                    | -0.36229             | -0.36229             | 0                    | 0                                            | 1.32010                | 0.87495                | -15.55033                          | 79.78                                     | 100.22         | 38.00          | 1.56425   | 0.15529   |
| $R_2S=O$                                  | O              | 0                    | 0                    | 0                    | 0                    | 0                                            | 1.00000                | 0.91771                | -14.82575                          | 84.06                                     | 95.94          | 40.75          | 1.50400   | 0.09594   |
| $R-SO$                                    | S              | -0.36229             | -0.36229             | 0                    | 0                    | 0                                            | 1.32010                | 0.87495                | -15.55033                          | 129.35                                    | 50.65          | 53.36          | 1.17999   | 0.55472   |
| $H_3C-S-O$                                | C <sub>α</sub> | -0.36229             | 0                    | 0                    | 0                    | -151.97798                                   | 0.91771                | 0.89382                | -15.18804                          | -14.99717                                 | 130.19         | 54.24          | 1.09461   | 0.57809   |
| $H_3C-S-O$                                | C <sub>β</sub> | -0.36229             | -0.92918             | 0                    | 0                    | -152.90716                                   | 0.91771                | 0.84418                | -16.11722                          | -15.92636                                 | 128.05         | 52.03          | 1.15245   | 0.52026   |
| $C-H$ (CH <sub>3</sub> )                  | C              | -0.92918             | 0                    | 0                    | 0                    | -152.54487                                   | 0.91771                | 0.86359                | -15.75493                          | -15.56407                                 | 77.49          | 102.51         | 1.23564   | 0.18708   |
| $C-H$ (CH <sub>2</sub> )                  | C              | -0.92918             | -0.92918             | 0                    | 0                    | -153.47406                                   | 0.91771                | 0.81549                | -16.68412                          | -16.49325                                 | 68.47          | 111.53         | 1.55486   | 0.29933   |
| $C-H$ (CH)                                | C              | -0.92918             | -0.92918             | -0.92918             | 0                    | -154.40324                                   | 0.91771                | 0.77247                | -17.61330                          | -17.42244                                 | 61.10          | 118.90         | 1.42988   | 0.37226   |
| $H_3C-C-H_2-CH_2-$<br>(C-C (a))           | C <sub>α</sub> | -0.92918             | 0                    | 0                    | 0                    | -152.54487                                   | 0.91771                | 0.86359                | -15.75493                          | -15.56407                                 | 63.82          | 116.18         | 1.83879   | 0.38106   |
| $H_3C-C-H_2-CH_2-$<br>(C-C (b))           | C <sub>β</sub> | -0.92918             | -0.92918             | 0                    | 0                    | -153.47406                                   | 0.91771                | 0.81549                | -16.68412                          | -16.49325                                 | 56.41          | 123.59         | 1.90890   | 0.45117   |
| $R-H_2C-C(H_2-C-R)HCH_2-$<br>(C-C (c))    | C <sub>α</sub> | -0.92918             | -0.92918             | -0.92918             | 0                    | -154.40324                                   | 0.91771                | 0.77247                | -17.61330                          | -17.42244                                 | 48.30          | 131.70         | 1.97162   | 0.51388   |
| $R-H_2C-C(H_2-C-R)HCH_2-$<br>(C-C (d))    | C <sub>β</sub> | -0.92918             | -0.92918             | -0.92918             | -0.72457             | -154.71860                                   | 0.91771                | 0.75889                | -17.92866                          | -17.73779                                 | 48.21          | 131.79         | 1.95734   | 0.50570   |
| $isoC_6H_5-C(H_2-C-R)HCH_2-$<br>(C-C (e)) | C <sub>α</sub> | -0.92918             | -0.92918             | -0.92918             | 0                    | -154.40324                                   | 0.91771                | 0.77247                | -17.61330                          | -17.42244                                 | 48.30          | 131.70         | 1.97162   | 0.51388   |
| $isoC_6H_5-C(H_2-C-R)HCH_2-$<br>(C-C (f)) | C <sub>β</sub> | -0.72457             | -0.72457             | -0.72457             | -0.72457             | -154.51399                                   | 0.91771                | 0.76765                | -17.92866                          | -17.73779                                 | 50.04          | 129.96         | 1.94462   | 0.49298   |
| $isoC_6H_5-C(H_2-C-R)HCH_2-$<br>(C-C (g)) | C <sub>α</sub> | -0.72457             | -0.92918             | -0.92918             | 0                    | -154.19863                                   | 0.91771                | 0.78155                | -17.40669                          | -17.21783                                 | 52.78          | 127.22         | 1.93445   | 0.47279   |
| $isoC_6H_5-C(H_2-C-R)HCH_2-$<br>(C-C (h)) | C <sub>β</sub> | -0.72457             | -0.72457             | -0.72457             | -0.72457             | -154.51399                                   | 0.91771                | 0.76765                | -17.92866                          | -17.73779                                 | 50.04          | 129.96         | 1.94462   | 0.49298   |

Table 15.168. The energy parameters (eV) of functional groups of alkyl sulfoxides.

| Parameters | C-S Group | SO Group | CH <sub>3</sub> Group | CH <sub>2</sub> Group | C-H Group | C-C (a) Group | C-C (b) Group | C-C (c) Group | C-C (d) Group | C-C (e) Group | C-C (f) Group |
|------------|-----------|----------|-----------------------|-----------------------|-----------|---------------|---------------|---------------|---------------|---------------|---------------|
| $\eta_1$   | 1         | 2        | 3                     | 2                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $\eta_2$   | 0         | 0        | 2                     | 1                     | 0         | 0             | 0             | 0             | 0             | 0             | 0             |
| $\eta_3$   | 0         | 0        | 0                     | 0                     | 0         | 0             | 0             | 0             | 0             | 0             | 0             |
| $C_1$      | 0.5       | 0.5      | 0.75                  | 0.75                  | 0.75      | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           |
| $C_2$      | 0.66951   | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_3$      | 1         | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_4$      | 1         | 1.20632  | 0.91771               | 0.91771               | 0.91771   | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       |
| $C_5$      | 0         | 0        | 0                     | 1                     | 1         | 0             | 0             | 0             | 1             | 1             | 0             |
| $C_6$      | 2         | 4        | 1                     | 1                     | 1         | 2             | 2             | 2             | 2             | 2             | 2             |
| $C_7$      | 0         | 1        | 3                     | 2                     | 1         | 0             | 0             | 0             | 0             | 0             | 0             |
| $C_{10}$   | 0.5       | 0.5      | 0.75                  | 0.75                  | 0.75      | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           |
| $C_{10a}$  | 0.66951   | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10b}$  | 1         | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10c}$  | 1         | 1.20632  | 0.91771               | 0.91771               | 0.91771   | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       |
| $C_{10d}$  | 0         | 0        | 0                     | 1                     | 1         | 0             | 0             | 0             | 1             | 1             | 0             |
| $C_{10e}$  | 2         | 4        | 1                     | 1                     | 1         | 2             | 2             | 2             | 2             | 2             | 2             |
| $C_{10f}$  | 0         | 1        | 3                     | 2                     | 1         | 0             | 0             | 0             | 0             | 0             | 0             |
| $C_{10g}$  | 0.5       | 0.5      | 0.75                  | 0.75                  | 0.75      | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           |
| $C_{10h}$  | 0.66951   | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10i}$  | 1         | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10j}$  | 1         | 1.20632  | 0.91771               | 0.91771               | 0.91771   | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       |
| $C_{10k}$  | 0         | 0        | 0                     | 1                     | 1         | 0             | 0             | 0             | 1             | 1             | 0             |
| $C_{10l}$  | 2         | 4        | 1                     | 1                     | 1         | 2             | 2             | 2             | 2             | 2             | 2             |
| $C_{10m}$  | 0         | 1        | 3                     | 2                     | 1         | 0             | 0             | 0             | 0             | 0             | 0             |
| $C_{10n}$  | 0.5       | 0.5      | 0.75                  | 0.75                  | 0.75      | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           |
| $C_{10o}$  | 0.66951   | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10p}$  | 1         | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10q}$  | 1         | 1.20632  | 0.91771               | 0.91771               | 0.91771   | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       |
| $C_{10r}$  | 0         | 0        | 0                     | 1                     | 1         | 0             | 0             | 0             | 1             | 1             | 0             |
| $C_{10s}$  | 2         | 4        | 1                     | 1                     | 1         | 2             | 2             | 2             | 2             | 2             | 2             |
| $C_{10t}$  | 0         | 1        | 3                     | 2                     | 1         | 0             | 0             | 0             | 0             | 0             | 0             |
| $C_{10u}$  | 0.5       | 0.5      | 0.75                  | 0.75                  | 0.75      | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           |
| $C_{10v}$  | 0.66951   | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10w}$  | 1         | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10x}$  | 1         | 1.20632  | 0.91771               | 0.91771               | 0.91771   | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       |
| $C_{10y}$  | 0         | 0        | 0                     | 1                     | 1         | 0             | 0             | 0             | 1             | 1             | 0             |
| $C_{10z}$  | 2         | 4        | 1                     | 1                     | 1         | 2             | 2             | 2             | 2             | 2             | 2             |
| $C_{10aa}$ | 0         | 1        | 3                     | 2                     | 1         | 0             | 0             | 0             | 0             | 0             | 0             |
| $C_{10ab}$ | 0.5       | 0.5      | 0.75                  | 0.75                  | 0.75      | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           |
| $C_{10ac}$ | 0.66951   | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10ad}$ | 1         | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10ae}$ | 1         | 1.20632  | 0.91771               | 0.91771               | 0.91771   | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       |
| $C_{10af}$ | 0         | 0        | 0                     | 1                     | 1         | 0             | 0             | 0             | 1             | 1             | 0             |
| $C_{10ag}$ | 2         | 4        | 1                     | 1                     | 1         | 2             | 2             | 2             | 2             | 2             | 2             |
| $C_{10ah}$ | 0         | 1        | 3                     | 2                     | 1         | 0             | 0             | 0             | 0             | 0             | 0             |
| $C_{10ai}$ | 0.5       | 0.5      | 0.75                  | 0.75                  | 0.75      | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           |
| $C_{10aj}$ | 0.66951   | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10ak}$ | 1         | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10al}$ | 1         | 1.20632  | 0.91771               | 0.91771               | 0.91771   | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       |
| $C_{10am}$ | 0         | 0        | 0                     | 1                     | 1         | 0             | 0             | 0             | 1             | 1             | 0             |
| $C_{10an}$ | 2         | 4        | 1                     | 1                     | 1         | 2             | 2             | 2             | 2             | 2             | 2             |
| $C_{10ao}$ | 0         | 1        | 3                     | 2                     | 1         | 0             | 0             | 0             | 0             | 0             | 0             |
| $C_{10ap}$ | 0.5       | 0.5      | 0.75                  | 0.75                  | 0.75      | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           |
| $C_{10aq}$ | 0.66951   | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10ar}$ | 1         | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10as}$ | 1         | 1.20632  | 0.91771               | 0.91771               | 0.91771   | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       |
| $C_{10at}$ | 0         | 0        | 0                     | 1                     | 1         | 0             | 0             | 0             | 1             | 1             | 0             |
| $C_{10au}$ | 2         | 4        | 1                     | 1                     | 1         | 2             | 2             | 2             | 2             | 2             | 2             |
| $C_{10av}$ | 0         | 1        | 3                     | 2                     | 1         | 0             | 0             | 0             | 0             | 0             | 0             |
| $C_{10aw}$ | 0.5       | 0.5      | 0.75                  | 0.75                  | 0.75      | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           |
| $C_{10ax}$ | 0.66951   | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10ay}$ | 1         | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10az}$ | 1         | 1.20632  | 0.91771               | 0.91771               | 0.91771   | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       |
| $C_{10ba}$ | 0         | 0        | 0                     | 1                     | 1         | 0             | 0             | 0             | 1             | 1             | 0             |
| $C_{10bb}$ | 2         | 4        | 1                     | 1                     | 1         | 2             | 2             | 2             | 2             | 2             | 2             |
| $C_{10bc}$ | 0         | 1        | 3                     | 2                     | 1         | 0             | 0             | 0             | 0             | 0             | 0             |
| $C_{10bd}$ | 0.5       | 0.5      | 0.75                  | 0.75                  | 0.75      | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           |
| $C_{10be}$ | 0.66951   | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10bf}$ | 1         | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10bg}$ | 1         | 1.20632  | 0.91771               | 0.91771               | 0.91771   | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       |
| $C_{10bh}$ | 0         | 0        | 0                     | 1                     | 1         | 0             | 0             | 0             | 1             | 1             | 0             |
| $C_{10bi}$ | 2         | 4        | 1                     | 1                     | 1         | 2             | 2             | 2             | 2             | 2             | 2             |
| $C_{10bj}$ | 0         | 1        | 3                     | 2                     | 1         | 0             | 0             | 0             | 0             | 0             | 0             |
| $C_{10bk}$ | 0.5       | 0.5      | 0.75                  | 0.75                  | 0.75      | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           |
| $C_{10bl}$ | 0.66951   | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10bm}$ | 1         | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10bn}$ | 1         | 1.20632  | 0.91771               | 0.91771               | 0.91771   | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       |
| $C_{10bo}$ | 0         | 0        | 0                     | 1                     | 1         | 0             | 0             | 0             | 1             | 1             | 0             |
| $C_{10bp}$ | 2         | 4        | 1                     | 1                     | 1         | 2             | 2             | 2             | 2             | 2             | 2             |
| $C_{10bq}$ | 0         | 1        | 3                     | 2                     | 1         | 0             | 0             | 0             | 0             | 0             | 0             |
| $C_{10br}$ | 0.5       | 0.5      | 0.75                  | 0.75                  | 0.75      | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           |
| $C_{10bs}$ | 0.66951   | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10bt}$ | 1         | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10bu}$ | 1         | 1.20632  | 0.91771               | 0.91771               | 0.91771   | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       |
| $C_{10bv}$ | 0         | 0        | 0                     | 1                     | 1         | 0             | 0             | 0             | 1             | 1             | 0             |
| $C_{10bw}$ | 2         | 4        | 1                     | 1                     | 1         | 2             | 2             | 2             | 2             | 2             | 2             |
| $C_{10bx}$ | 0         | 1        | 3                     | 2                     | 1         | 0             | 0             | 0             | 0             | 0             | 0             |
| $C_{10by}$ | 0.5       | 0.5      | 0.75                  | 0.75                  | 0.75      | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           |
| $C_{10bz}$ | 0.66951   | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10ca}$ | 1         | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10cb}$ | 1         | 1.20632  | 0.91771               | 0.91771               | 0.91771   | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       |
| $C_{10cc}$ | 0         | 0        | 0                     | 1                     | 1         | 0             | 0             | 0             | 1             | 1             | 0             |
| $C_{10cd}$ | 2         | 4        | 1                     | 1                     | 1         | 2             | 2             | 2             | 2             | 2             | 2             |
| $C_{10ce}$ | 0         | 1        | 3                     | 2                     | 1         | 0             | 0             | 0             | 0             | 0             | 0             |
| $C_{10cf}$ | 0.5       | 0.5      | 0.75                  | 0.75                  | 0.75      | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           |
| $C_{10cg}$ | 0.66951   | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10ch}$ | 1         | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10ci}$ | 1         | 1.20632  | 0.91771               | 0.91771               | 0.91771   | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       |
| $C_{10cj}$ | 0         | 0        | 0                     | 1                     | 1         | 0             | 0             | 0             | 1             | 1             | 0             |
| $C_{10ck}$ | 2         | 4        | 1                     | 1                     | 1         | 2             | 2             | 2             | 2             | 2             | 2             |
| $C_{10cl}$ | 0         | 1        | 3                     | 2                     | 1         | 0             | 0             | 0             | 0             | 0             | 0             |
| $C_{10cm}$ | 0.5       | 0.5      | 0.75                  | 0.75                  | 0.75      | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           |
| $C_{10cn}$ | 0.66951   | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10co}$ | 1         | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10cp}$ | 1         | 1.20632  | 0.91771               | 0.91771               | 0.91771   | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       |
| $C_{10cq}$ | 0         | 0        | 0                     | 1                     | 1         | 0             | 0             | 0             | 1             | 1             | 0             |
| $C_{10cr}$ | 2         | 4        | 1                     | 1                     | 1         | 2             | 2             | 2             | 2             | 2             | 2             |
| $C_{10cs}$ | 0         | 1        | 3                     | 2                     | 1         | 0             | 0             | 0             | 0             | 0             | 0             |
| $C_{10ct}$ | 0.5       | 0.5      | 0.75                  | 0.75                  | 0.75      | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           |
| $C_{10cu}$ | 0.66951   | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10cv}$ | 1         | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10cw}$ | 1         | 1.20632  | 0.91771               | 0.91771               | 0.91771   | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       |
| $C_{10cx}$ | 0         | 0        | 0                     | 1                     | 1         | 0             | 0             | 0             | 1             | 1             | 0             |
| $C_{10cy}$ | 2         | 4        | 1                     | 1                     | 1         | 2             | 2             | 2             | 2             | 2             | 2             |
| $C_{10cz}$ | 0         | 1        | 3                     | 2                     | 1         | 0             | 0             | 0             | 0             | 0             | 0             |
| $C_{10da}$ | 0.5       | 0.5      | 0.75                  | 0.75                  | 0.75      | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           |
| $C_{10db}$ | 0.66951   | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10dc}$ | 1         | 1        | 1                     | 1                     | 1         | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_{10dd}$ | 1         | 1.20632  | 0.91771               | 0.91771               | 0.91771   | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       |
| $C_{10de}$ | 0         | 0        | 0                     | 1                     | 1         | 0             | 0             | 0             | 1             | 1             | 0             |
| $C_{10df}$ | 2         | 4        | 1                     | 1                     | 1         | 2             | 2             | 2             | 2             | 2             | 2             |
| $C_{10dg}$ | 0         | 1        | 3                     | 2                     | 1         | 0             | 0             | 0             | 0             | 0             | 0             |
| $C_{10dh}$ | 0.5       | 0.5      | 0.75                  | 0.75                  | 0.75      | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           |
| $C_{10di}$ | 0.66951   | 1        | 1                     | 1                     | 1</       |               |               |               |               |               |               |



# SULFOXIDES ( $C_nH_{2n+2}(SO)_m$ , $n = 2, 3, 4, 5, \dots, \infty$ )

The alkyl sulfoxides,  $C_nH_{2n+2}(SO)_m$ , comprise a  $C-SO-C$  moiety that comprises  $C-S$  and  $SO$  functional groups. The alkyl portion of the alkyl sulfoxide may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in sulfoxides are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is  $1s^2 2s^2 2p^4$ , and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state  $^3P_2$ . The  $SO$  functional group comprises a double bond between the two unpaired electrons of  $O$ . The sulfur atom is energy matched to the  $C2sp^3$  HO. In alkyl sulfoxides, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)), and the  $S$  AO has an initial energy of  $E(S) = -10.36001 \text{ eV}$  [38]. To meet the equipotential condition of the union of the  $S=O$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the  $S=O$ -bond MO given by Eqs. (15.68) and (15.70) is

$$\begin{aligned} c_2(O \text{ to } S3sp^3 \text{ to } C2sp^3 HO) &= \frac{E(O)}{E(S)} c_2(C2sp^3 HO) \\ &= \frac{-13.61806 \text{ eV}}{-10.36001 \text{ eV}} (0.91771) \\ &= 1.20632 \end{aligned} \quad (15.128)$$

The  $S$  atom also forms a single bond with each of the  $C2sp^3$  HOs of the two  $C-S$  groups. The formation of these bonds is permitted by the hybridization of the four electrons of the  $S3p$  shell to give the orbital arrangement:

$$\begin{array}{cccc} & \text{3sp}^3 \text{ state} & & \\ \uparrow & \uparrow & \uparrow & \uparrow \\ 0,0 & 1,-1 & 1,0 & 1,1 \end{array} \quad (15.129)$$

where the quantum numbers ( $\ell, m_\ell$ ) are below each electron. The  $3s$  shell remains unchanged. Then, the Coulombic energy  $E_{Coulomb}(S, 3sp^3)$  of the outer electron of the  $S3sp^3$  shell given by Eq. (15.118) with  $r_{3sp^3} = 1.17585a_0$  (Eq. (15.119)) is  $-11.57099 \text{ eV}$ . Using Eq. (15.16) with the radius of the sulfur atom  $r_{16} = 1.32010a_0$  given by Eq. (10.341), the energy  $E(S3sp^3)$  of the 5 outer electron of the  $S3sp^3$  shell is given by the sum of  $E_{Coulomb}(S3sp^3)$  and  $E(magnetic)$ :

$$\begin{aligned} E(S3sp^3) &= \frac{-e^2}{8\pi\epsilon_0 r_{3sp^3}} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 r_{16}^3} \\ &= \frac{-e^2}{8\pi\epsilon_0 1.17585a_0} + \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 (1.32010a_0)^3} \\ &= -11.57099 \text{ eV} + 0.04973 \\ &= -11.52126 \text{ eV} \end{aligned} \quad (15.130)$$

Then, the hybridization energy  $E_{hybridization}(S3sp^3)$  of the  $S3sp^3$  HO is

$$\begin{aligned} E_{hybridization}(S3sp^3) &= E(S3sp^3) - E(S) \\ &= -11.52126 \text{ eV} - 10.36001 \text{ eV} \\ &= -1.16125 \text{ eV} \end{aligned} \quad (15.131)$$

The  $SO$  group is matched to the  $C-S$  group with which it shares the common hybridized  $S$  atom. Consequently,  $E_{hybridization}(S3sp^3)$  is subtracted from  $E_r(Group)$  in the determination of  $E_D(Group)$  (Eq. 15.56). Furthermore, the energy of the  $S=O$ -bond MO is the sum of the component energies of the  $H_2$ -type ellipsoidal MO given in Eq. (15.42) with the energy matched to the final energy of the hybridized  $S$  atom such that

$$E(AO / HO) = E(S3sp^3) = -11.52126 \text{ eV} \quad \text{a n d}$$

$$15 \quad \Delta E_{H_2MO}(AO / HO) = E_{hybridization}(S3sp^3) = -1.16125 \text{ eV} . \quad \text{T h e n ,}$$

$E_r(AO / HO) = E(S) = -10.36001 \text{ eV}$ . Also,  $E_r(atom - atom, msp^3.AO)$  of the  $S=O$  bond is zero since there are no bonds with a  $C2sp^3$  HO.

The  $C-S$  group is solved as an energy minimum by hybridizing the  $2s$  and  $2p$  AOs of the  $C$  atom to form a single  $2sp^3$  shell and by hybridizing the four  $S3p$  electrons to form a  $S3sp^3$  shell, and the sharing of electrons between the  $C2sp^3$  HO and the  $S3sp^3$  HO to form a MO permits each participating orbital to decrease in radius and energy. Using the Coulombic

energy of the  $S3sp^3$  shell,  $E_{Coulomb}(S3sp^3)$  given by Eq. (15.120) in Eq. (15.63), the  $S3sp^3$ -shell hybridization factor,  $c_2(S3sp^3)$ , is

$$c_2(S3sp^3) = \frac{E_{Coulomb}(S3sp^3)}{E(H)} = \frac{-11.57099 \text{ eV}}{-13.60580 \text{ eV}} = 0.85045 \quad (15.132)$$

As in the case of thiols, sulfides, and disulfides, the energy of sulfur is less than the  
5 Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). Thus,  $c_1$  and  $c_2$  are equal to one in Eq. (15.52), and the energy matching condition is determined by the  $C_2$  parameter. In alkyl sulfoxides, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)) and the  $S3sp^3$  HO has an energy of  $E(S3sp^3) = -11.52126 \text{ eV}$  (Eq. (15.130)). To meet the  
10 equipotential condition of the union of the  $C-S$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $C_2$  of Eq. (15.52) for the  $C-S$ -bond MO given by Eqs. (15.68) and (15.70) is

$$C_2(C2sp^3 HO \text{ to } S3sp^3) = \frac{E(S3sp^3)}{E(C, 2sp^3)} c_2(S3sp^3) = \frac{-11.52126 \text{ eV}}{-14.63489 \text{ eV}} (0.85045) = 0.66951 \quad (15.133)$$

As in the case of thiols, sulfides, and disulfides, with the energy of  $S$  matched to the  
15 Coulombic energy between the electron and proton of  $H$ , the energy of the  $C-S$ -bond MO is the sum of the component energies of the  $H_2$ -type ellipsoidal MO given in Eq. (15.42) with

$$E(AO/HO) = 0 \quad \text{and} \quad E_T(AO/HO) = \Delta E_{H_2MO}(AO/HO). \quad \text{For sulfoxides,}$$

$$\Delta E_{H_2MO}(AO/HO) = -0.72457 \text{ eV}. \quad \text{Further equivalently,}$$

$$E_T(atom - atom, msp^3 AO) = -0.72457 \text{ eV} \quad (\text{Eq. (14.151)}).$$

20 The symbols of the functional groups of branched-chain alkyl sulfoxides are given in Table 15.165. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfoxides are given in Tables 15.166, 15.167, and 15.168, respectively. Consider that the  $C-S$  bond is along the  $x$  axis in the  $xy$ -plane. The  $S$  nucleus is at the focus  $+c$  and the  $C$  nucleus is at the focus  $-c$ . The  
25 elliptic angle  $\theta'$  is taken as counterclockwise from the  $x$ -axis for  $S$  and as clockwise from the  $-x$ -axis for  $C$ . The total energy of each alkyl sulfoxide given in Table 15.169 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.168 corresponding to functional-

group composition of the molecule. The bond angle parameters of alkyl sulfoxides determined using Eqs. (15.79-15.108) are given in Table 15.170.

Table 15.165. The symbols of functional groups of alkyl sulfoxides.

| Functional Group      | Group Symbol |
|-----------------------|--------------|
| C-S                   | $C-S$        |
| SO                    | $SO$         |
| CH <sub>3</sub> group | $C-H (CH_3)$ |
| CH <sub>2</sub> group | $C-H (CH_2)$ |
| CH                    | $C-H$        |
| CC bond (n-C)         | $C-C (a)$    |
| CC bond (iso-C)       | $C-C (b)$    |
| CC bond (tert-C)      | $C-C (c)$    |
| CC (iso to iso-C)     | $C-C (d)$    |
| CC (t to t-C)         | $C-C (e)$    |
| CC (t to iso-C)       | $C-C (f)$    |



Table 15.166. The geometrical bond parameters of alkyl sulfoxides and experimental values [1].

| Parameter                   | C-S Group                  | S-O Group                  | C-H (CH <sub>3</sub> ) Group | C-H (CH <sub>2</sub> ) Group | C-C (a) Group   | C-C (b) Group   | C-C (c) Group   | C-C (d) Group   | C-C (e) Group   | C-C (f) Group   |
|-----------------------------|----------------------------|----------------------------|------------------------------|------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $\alpha$ (°)                | 1.87325                    | 1.98517                    | 1.64920                      | 1.67122                      | 2.12499         | 2.12499         | 2.10725         | 2.12499         | 2.10725         | 2.10725         |
| $\epsilon'$ (°)             | 1.67271                    | 1.40896                    | 1.04856                      | 1.05553                      | 1.45744         | 1.45744         | 1.45164         | 1.45744         | 1.45164         | 1.45164         |
| Bond Length 2c' (Å)         | 1.77031                    | 1.49118                    | 1.10974                      | 1.11713                      | 1.54280         | 1.54280         | 1.53635         | 1.54280         | 1.53635         | 1.53635         |
| Exp. Bond Length (Å)        | 1.799 (dimethyl sulfoxide) | 1.485 (dimethyl sulfoxide) | 1.107 (C-H propane)          | 1.107 (C-H propane)          | 1.532 (propane) | 1.532 (propane) | 1.532 (propane) | 1.532 (propane) | 1.532 (propane) | 1.532 (propane) |
| $h_{s,c}$ (a <sub>c</sub> ) | 0.84328                    | 1.39847                    | 1.27295                      | 1.29569                      | 1.54616         | 1.54616         | 1.52750         | 1.54616         | 1.52750         | 1.52750         |
| $\epsilon$                  | 0.89294                    | 0.70974                    | 0.63580                      | 0.63159                      | 0.68600         | 0.68600         | 0.68888         | 0.68600         | 0.68888         | 0.68888         |

Table 15.167. The MO to HO intercept geometrical bond parameters of alkyl sulfoxides.  $R_s, R', R''$  are H or alkyl groups.  $E_p$  is  $E_p(\text{atom} - \text{atom}, \text{msp}, \text{AO})$ .

| Bond                                                                     | Atom           | $E_p$ (eV) Bond 1 | $E_p$ (eV) Bond 2 | $E_p$ (eV) Bond 3 | $E_p$ (eV) Bond 4 | $E_p$ (eV) Final Total | $r_{\text{final}}$ (a <sub>c</sub> ) | $r_{\text{final}}$ (a <sub>c</sub> ) | $E_{\text{calculated}}$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ (a <sub>c</sub> ) | $d_2$ (a <sub>c</sub> ) |
|--------------------------------------------------------------------------|----------------|-------------------|-------------------|-------------------|-------------------|------------------------|--------------------------------------|--------------------------------------|------------------------------------|------------------------|---------------|----------------|----------------|-------------------------|-------------------------|
| $R_s S = O$                                                              | S              | 0                 | -0.36229          | -0.36229          | 0                 | 1.32010                | 0.87495                              | 0.87495                              | -15.50033                          |                        | 79.78         | 100.22         | 38.00          | 1.56425                 | 0.15529                 |
| $R_s S = O$                                                              | O              | 0                 | 0                 | 0                 | 0                 | 1.00000                | 0.91771                              | 0.91771                              | -14.8275                           |                        | 84.06         | 95.94          | 40.75          | 1.50400                 | 0.09504                 |
| $R_s - SO$                                                               | S              | -0.36229          | -0.36229          | 0                 | 0                 | 1.32010                | 0.87495                              | 0.87495                              | -15.50033                          |                        | 129.35        | 50.65          | 53.36          | 1.11799                 | 0.54472                 |
| $H_s C_s - S(O) - C_s H_s C H_2 R$                                       | C <sub>s</sub> | -0.36229          | 0                 | 0                 | 0                 | -151.97798             | 0.91771                              | 0.89582                              | -15.18804                          | -14.99717              | 130.19        | 49.81          | 34.24          | 1.09461                 | 0.37809                 |
| $H_s C_s - S(O) - C_s H_s C H_2 R$                                       | C <sub>s</sub> | -0.36229          | -0.92918          | 0                 | 0                 | -152.90716             | 0.91771                              | 0.84418                              | -16.11722                          | -15.92636              | 128.05        | 51.95          | 52.03          | 1.15245                 | 0.52026                 |
| C-H (CH <sub>3</sub> )                                                   | C              | -0.92918          | 0                 | 0                 | 0                 | -152.54487             | 0.91771                              | 0.86359                              | -15.75093                          | -15.56407              | 77.49         | 102.51         | 41.48          | 1.23564                 | 0.18708                 |
| C-H (CH <sub>2</sub> )                                                   | C              | -0.92918          | -0.92918          | 0                 | 0                 | -153.47406             | 0.91771                              | 0.81549                              | -16.08412                          | -16.49325              | 68.47         | 111.55         | 35.84          | 1.53486                 | 0.29933                 |
| C-H (CH)                                                                 | C              | -0.92918          | -0.92918          | -0.92918          | 0                 | -154.40324             | 0.91771                              | 0.77247                              | -17.61330                          | -17.42244              | 61.10         | 118.90         | 31.37          | 1.42988                 | 0.37326                 |
| $H_s C_s C_s H_s C H_2 -$<br>(C-C (a))                                   | C <sub>s</sub> | -0.92918          | 0                 | 0                 | 0                 | -152.54487             | 0.91771                              | 0.86359                              | -15.75093                          | -15.56407              | 63.82         | 116.18         | 30.08          | 1.83879                 | 0.38106                 |
| $H_s C_s C_s H_s C H_2 -$<br>(C-C (a))                                   | C <sub>s</sub> | -0.92918          | -0.92918          | 0                 | 0                 | -153.47406             | 0.91771                              | 0.81549                              | -16.08412                          | -16.49325              | 56.41         | 125.59         | 26.06          | 1.90890                 | 0.45117                 |
| $R - H_s C_s C_s (H_s C_s - R') H C H_2 -$<br>(C-C (b))                  | C <sub>s</sub> | -0.92918          | -0.92918          | -0.92918          | 0                 | -154.40324             | 0.91771                              | 0.77247                              | -17.61330                          | -17.42244              | 48.30         | 131.70         | 21.90          | 1.97162                 | 0.51388                 |
| $R - H_s C_s C_s (R' - H_s C_s) C_s (R' - H_s C_s) C H_2 -$<br>(C-C (c)) | C <sub>s</sub> | -0.92918          | -0.92918          | -0.92918          | 0                 | -154.40324             | 0.91771                              | 0.77247                              | -17.61330                          | -17.42244              | 48.30         | 131.70         | 21.90          | 1.97162                 | 0.51388                 |
| $iso C_s C_s (H_s C_s - R') H C H_2 -$<br>(C-C (d))                      | C <sub>s</sub> | -0.92918          | -0.92918          | -0.92918          | -0.72457          | -154.71860             | 0.91771                              | 0.75889                              | -17.92866                          | -17.73779              | 48.21         | 131.79         | 21.74          | 1.95734                 | 0.50570                 |
| $iso C_s C_s (R' - H_s C_s) C_s (R' - H_s C_s) C H_2 -$<br>(C-C (e))     | C <sub>s</sub> | -0.92918          | -0.92918          | -0.92918          | 0                 | -154.40324             | 0.91771                              | 0.77247                              | -17.61330                          | -17.42244              | 48.30         | 131.70         | 21.90          | 1.97162                 | 0.51388                 |
| $iso C_s C_s (H_s C_s - R') H C H_2 -$<br>(C-C (f))                      | C <sub>s</sub> | -0.92918          | -0.92918          | -0.92918          | -0.72457          | -154.71860             | 0.91771                              | 0.75889                              | -17.92866                          | -17.73779              | 50.04         | 129.96         | 22.66          | 1.94462                 | 0.49298                 |
| $iso C_s C_s (R' - H_s C_s) C_s (R' - H_s C_s) C H_2 -$<br>(C-C (f))     | C <sub>s</sub> | -0.92918          | -0.92918          | -0.92918          | 0                 | -154.40324             | 0.91771                              | 0.77247                              | -17.61330                          | -17.42244              | 52.78         | 127.22         | 24.04          | 1.92443                 | 0.47279                 |
| $iso C_s C_s (R' - H_s C_s) C_s (R' - H_s C_s) C H_2 -$<br>(C-C (f))     | C <sub>s</sub> | -0.92918          | -0.92918          | -0.92918          | -0.72457          | -154.71860             | 0.91771                              | 0.75889                              | -17.92866                          | -17.73779              | 50.04         | 129.96         | 22.66          | 1.94462                 | 0.49298                 |

Table 15.168. The energy parameters (eV) of functional groups of alkyl sulfoxides.

| Parameters                        | C-S Group | SO Group  | CH <sub>3</sub> Group | CH <sub>2</sub> Group | C-H Group | C-C (a) Group  | C-C (b) Group  | C-C (c) Group  | C-C (d) Group  | C-C (e) Group  | C-C (f) Group  |
|-----------------------------------|-----------|-----------|-----------------------|-----------------------|-----------|----------------|----------------|----------------|----------------|----------------|----------------|
| $\eta_1$                          | 1         | 2         | 3                     | 2                     | 1         | 1              | 1              | 1              | 1              | 1              | 1              |
| $\eta_2$                          | 0         | 0         | 2                     | 1                     | 0         | 0              | 0              | 0              | 0              | 0              | 0              |
| $\eta_3$                          | 0         | 0         | 0                     | 0                     | 0         | 0              | 0              | 0              | 0              | 0              | 0              |
| $C_1$                             | 0.5       | 0.5       | 0.75                  | 0.75                  | 0.75      | 0.5            | 0.5            | 0.5            | 0.5            | 0.5            | 0.5            |
| $C_2$                             | 0.66951   | 1         | 1                     | 1                     | 1         | 1              | 1              | 1              | 1              | 1              | 1              |
| $C_3$                             | 1         | 1         | 1                     | 1                     | 1         | 1              | 1              | 1              | 1              | 1              | 1              |
| $C_4$                             | 1         | 1.20632   | 0.91771               | 0.91771               | 0.91771   | 0.91771        | 0.91771        | 0.91771        | 0.91771        | 0.91771        | 0.91771        |
| $C_5$                             | 0         | 0         | 0                     | 1                     | 1         | 0              | 0              | 0              | 1              | 1              | 0              |
| $C_6$                             | 2         | 4         | 1                     | 1                     | 1         | 2              | 2              | 2              | 2              | 2              | 2              |
| $C_7$                             | 0         | 1         | 3                     | 2                     | 1         | 0              | 0              | 0              | 0              | 0              | 0              |
| $C_{10}$                          | 0.5       | 0.5       | 0.75                  | 0.75                  | 0.75      | 0.5            | 0.5            | 0.5            | 0.5            | 0.5            | 0.5            |
| $C_{10}$                          | 0.66951   | 1         | 1                     | 1                     | 1         | 1              | 1              | 1              | 1              | 1              | 1              |
| $V_1$ (eV)                        | -46.73032 | -82.63003 | -107.32728            | -70.41425             | -35.12015 | -28.79214      | -28.79214      | -29.10112      | -28.79214      | -29.10112      | -29.10112      |
| $V_2$ (eV)                        | 8.13401   | 19.31325  | 38.92728              | 25.78002              | 12.87680  | 9.33532        | 9.33532        | 9.37273        | 9.33532        | 9.37273        | 9.37273        |
| $T$ (eV)                          | 12.47306  | 20.81183  | 32.55914              | 21.06675              | 10.48382  | 6.77464        | 6.77464        | 6.90500        | 6.77464        | 6.90500        | 6.90500        |
| $V_3$ (eV)                        | -6.23653  | -10.40592 | -16.26957             | -10.53337             | -5.24291  | -3.38732       | -3.38732       | -3.45250       | -3.38732       | -3.45250       | -3.45250       |
| $E_{10}$ (eV)                     | 0         | -11.32126 | -15.56407             | -15.56407             | -14.63489 | -15.56407      | -15.56407      | -15.35946      | -15.56407      | -15.35946      | -15.35946      |
| $\Delta E_{10}$ (eV)              | -0.72457  | -1.16125  | 0                     | 0                     | 0         | 0              | 0              | 0              | 0              | 0              | 0              |
| $E_{10}$ (eV)                     | 0.72457   | -10.36001 | -15.56407             | -15.56407             | -14.63489 | -15.56407      | -15.56407      | -15.35946      | -15.56407      | -15.35946      | -15.35946      |
| $E_{10}$ (eV)                     | -31.63551 | -63.27088 | -67.69451             | -49.66493             | -31.63553 | -31.63537      | -31.63537      | -31.63535      | -31.63537      | -31.63535      | -31.63535      |
| $E_{10}$ (eV)                     | -0.72457  | 0         | 0                     | 0                     | 0         | -1.85836       | -1.85836       | -1.44915       | -1.85836       | -1.44915       | -1.44915       |
| $E_{10}$ (eV)                     | -32.35994 | -63.27074 | -67.69450             | -49.66493             | -31.63537 | -33.49373      | -33.49373      | -33.08452      | -33.49373      | -33.08452      | -33.08452      |
| $\omega$ (10 <sup>15</sup> rad/s) | 30.8880   | 17.6762   | 24.9786               | 24.2751               | 24.1759   | 9.43699        | 9.43699        | 15.4846        | 9.43699        | 9.55643        | 9.55643        |
| $E_{10}$ (eV)                     | 20.33104  | 11.63476  | 16.40846              | 15.97831              | 15.91299  | 6.21159        | 6.21159        | 10.19220       | 6.21159        | 6.29021        | 6.29021        |
| $E_{10}$ (eV)                     | -0.28866  | -0.21348  | -0.25352              | -0.25017              | -0.24966  | -0.16515       | -0.16515       | -0.20896       | -0.16515       | -0.16416       | -0.16416       |
| $E_{10}$ (eV)                     | 0.08543   | 0.12832   | 0.35532               | 0.35532               | 0.35532   | 0.12312        | 0.17978        | 0.09944        | 0.12312        | 0.12312        | 0.12312        |
| $E_{10}$ (eV)                     | -0.24595  | -0.14932  | -0.22757              | -0.14502              | -0.07200  | (Eq. (13.458)) | (Eq. (13.458)) | (Eq. (13.458)) | (Eq. (13.458)) | (Eq. (13.458)) | (Eq. (13.458)) |
| $E_{10}$ (eV)                     | 0.14803   | 0.1441    | 0.14803               | 0.14803               | 0.14803   | -0.10359       | -0.07526       | -0.15924       | -0.10359       | -0.10260       | -0.10260       |
| $E_{10}$ (eV)                     | -32.60589 | -63.50937 | -67.92207             | -49.80996             | -31.70737 | -33.59732      | -33.59732      | -33.24376      | -33.59732      | -33.18712      | -33.18712      |
| $E_{10}$ (eV)                     | -14.63489 | -14.63489 | -14.63489             | -14.63489             | -14.63489 | -14.63489      | -14.63489      | -14.63489      | -14.63489      | -14.63489      | -14.63489      |
| $E_{10}$ (eV)                     | 0         | -1.16125  | -13.59844             | -13.59844             | -13.59844 | 0              | 0              | 0              | 0              | 0              | 0              |
| $E_{10}$ (eV)                     | 3.33611   | 3.86856   | 12.49186              | 7.83016               | 3.32601   | 4.32754        | 4.29921        | 3.97398        | 4.17951        | 3.62128        | 3.91734        |

Table 15.169. The total bond energies of alkyl sulfoxides calculated using the functional group composition and the energies of Table 15.168 compared to the experimental values [3].

| Formula                           | Name                  | C-S Group | SO Group | CH <sub>3</sub> Group | CH <sub>2</sub> Group | CH Group | C-C (a) | C-C (b) | C-C (c) | C-C (d) | C-C (e) | C-C (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|-----------------------------------|-----------------------|-----------|----------|-----------------------|-----------------------|----------|---------|---------|---------|---------|---------|---------|-----------------------------------|-------------------------------------|----------------|
| C <sub>2</sub> H <sub>4</sub> SO  | Dimethyl sulfoxide    | 2         | 1        | 2                     | 0                     | 0        | 0       | 0       | 0       | 0       | 0       | 0       | 33.52450                          | 33.433                              | -0.00033       |
| C <sub>2</sub> H <sub>6</sub> SO  | Diethyl sulfoxide     | 2         | 1        | 2                     | 2                     | 0        | 0       | 0       | 0       | 0       | 0       | 0       | 59.85990                          | 59.891                              | 0.00085        |
| C <sub>4</sub> H <sub>10</sub> SO | Diisopropyl sulfoxide | 2         | 1        | 2                     | 4                     | 0        | 0       | 0       | 0       | 0       | 0       | 0       | 84.15550                          | 84.294                              | 0.00165        |

Table 15.170. The bond angle parameters of alkyl sulfoxides and experimental values [1]. In the calculation of  $\theta_i$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{msp}^3 \text{AO})$ .

| Atoms of angle                | $2c_1'$<br>Bond 1<br>( $\theta_1$ ) | $2c_2'$<br>Bond 2<br>( $\theta_2$ ) | $2c_3'$<br>Terminal<br>Atom ( $\theta_3$ ) | $E_{\text{valence}}$<br>Atom 1 | Atom 1<br>Hybridization<br>Designation<br>(Table 15.3 A) | $E_{\text{valence}}$<br>Atom 2 | Atom 2<br>Hybridization<br>Designation<br>(Table 15.3 A) | $c_2$<br>Atom 1 | $c_2$<br>Atom 2<br>(Eq. 15.114) | $C_1$ | $C_2$ | $c_1$ | $c_2$   | $E_T$<br>(eV) | $\theta_i$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | Cal. $\theta$<br>( $^\circ$ ) | Exp. $\theta$<br>( $^\circ$ )                                                                                                 |
|-------------------------------|-------------------------------------|-------------------------------------|--------------------------------------------|--------------------------------|----------------------------------------------------------|--------------------------------|----------------------------------------------------------|-----------------|---------------------------------|-------|-------|-------|---------|---------------|----------------------------|----------------------------|----------------------------|-------------------------------|-------------------------------------------------------------------------------------------------------------------------------|
| $\angle C_1' C_2' C_3'$       | 3.34541                             | 3.34541                             | 4.9600                                     | -16.47951                      | 21                                                       | -16.47951                      | 21                                                       | 0.82562         | 0.82562                         | 1     | 1     | 1     | 0.82562 | -1.85836      |                            |                            |                            | 96.20                         | 96.6<br>(dimethyl sulfoxide)                                                                                                  |
| $\angle C_1' C_2' O$          | 3.34541                             | 2.81792                             | 4.9598                                     | -15.18004                      | 2                                                        | -15.18004                      | O                                                        | 0.83395         | 0.83395<br>(Eq. 15.114)         | 1     | 1     | 1     | 0.83395 | -1.65376      |                            |                            |                            | 106.88                        | 106.7<br>(dimethyl sulfoxide)                                                                                                 |
| Methylene<br>$\angle HC_1' H$ | 2.11106                             | 2.11106                             | 3.4252                                     | -15.75493                      | 7                                                        | H                              | H                                                        | 0.86359         | 1                               | 1     | 1     | 0.75  | 1.15796 | 0             |                            |                            |                            | 108.44                        | 107<br>(propane)                                                                                                              |
| $\angle C_1' C_2' C_3'$       |                                     |                                     |                                            |                                |                                                          |                                |                                                          |                 |                                 |       |       |       |         |               | 69.51                      |                            |                            | 110.49                        | 113.8<br>(isobutane)<br>110.8<br>(isobutane)<br>111.0<br>(isobutane)<br>111.4<br>(isobutane)<br>110.3<br>(dimethyl sulfoxide) |
| Methyl<br>$\angle HC_1' H$    | 2.09711                             | 2.09711                             | 3.4252                                     | -15.75493                      | 7                                                        | H                              | H                                                        | 0.86359         | 1                               | 1     | 1     | 0.75  | 1.15796 | 0             |                            |                            |                            | 109.50                        | 109.44<br>(propane)                                                                                                           |
| $\angle C_1' C_2' C_3'$       |                                     |                                     |                                            |                                |                                                          |                                |                                                          |                 |                                 |       |       |       |         |               | 70.56                      |                            |                            | 109.44                        |                                                                                                                               |
| $\angle C_1' C_2' H$          | 2.91547                             | 2.91547                             | 4.7958                                     | -16.60412                      | 25                                                       | $C_2'$                         | 25                                                       | 0.81549         | 0.81549                         | 1     | 1     | 1     | 0.81549 | -1.85836      |                            |                            |                            | 110.67                        | 110.8<br>(isobutane)                                                                                                          |
| iso $C_1'$                    | 2.91547                             | 2.11323                             | 4.1633                                     | -15.53033                      | 5                                                        | $C_1'$                         | 1                                                        | 0.87495         | 0.91771                         | 0.75  | 1     | 0.75  | 1.04887 | 0             |                            |                            |                            | 110.76                        |                                                                                                                               |
| iso $C_2'$                    | 2.91547                             | 2.09711                             | 4.1633                                     | -15.53033                      | 5                                                        | $C_2'$                         | 1                                                        | 0.87495         | 0.91771                         | 0.75  | 1     | 0.75  | 1.04887 | 0             |                            |                            |                            | 111.27                        | 111.4<br>(isobutane)                                                                                                          |
| tert $C_1'$                   | 2.90327                             | 2.90327                             | 4.7958                                     | -15.53033                      | 5                                                        | $C_1'$                         | 1                                                        | 0.87495         | 0.91771                         | 0.75  | 1     | 0.75  | 1.04887 | -1.85836      |                            |                            |                            | 111.27                        | 111.4<br>(isobutane)                                                                                                          |
| $\angle C_1' C_2' C_3'$       |                                     |                                     |                                            |                                |                                                          |                                |                                                          |                 |                                 |       |       |       |         |               | 72.50                      |                            |                            | 107.50                        |                                                                                                                               |

## DIMETHYL SULFOXIDE DIHEDRAL ANGLE

The dihedral angle  $\theta_{\angle S=O/CSC'}$  between the plane defined by the CSC MO comprising a linear combination of two  $S-C$ -bond MOs and a line defined by the  $S=O$ -bond MO where  $S$  is the central atom is calculated using the results given in Table 15.170 and Eqs. (15.105-15.108). The distance  $d_1$  along the bisector of  $\theta_{\angle CSC'}$  from  $S$  to the internuclear-distance line between  $C$  and  $C$ ,  $2c'_{C-C}$ , is given by

$$d_1 = 2c'_{S-C} \cos \frac{\theta_{\angle CSC'}}{2} = 4.9800a_0 \cos \frac{96.20^\circ}{2} = 2.23423a_0 \quad (15.134)$$

where  $2c'_{S-C}$  is the internuclear distance between  $S$  and  $C$ . The atoms  $C$ ,  $C$ , and  $O$  define the base of a pyramid. Then, the pyramidal angle  $\theta_{\angle COC'}$  can be solved from the internuclear distances between  $C$  and  $C$ ,  $2c'_{C-C}$ , and between  $C$  and  $O$ ,  $2c'_{C-O}$ , using the law of cosines (Eq. (15.106)):

$$\begin{aligned} \theta_{\angle COC'} &= \cos^{-1} \left( \frac{(2c'_{C-O})^2 + (2c'_{C-O})^2 - (2c'_{C-C})^2}{2(2c'_{C-O})(2c'_{C-O})} \right) \\ &= \cos^{-1} \left( \frac{(4.95984)^2 + (4.95984)^2 - (4.9800)^2}{2(4.95984)(4.95984)} \right) \\ &= 60.27^\circ \end{aligned} \quad (15.135)$$

Then, the distance  $d_2$  along the bisector of  $\theta_{\angle COC'}$  from  $O$  to the internuclear-distance line  $2c'_{C-C}$ , is given by

$$d_2 = 2c'_{C-O} \cos \frac{\theta_{\angle COC'}}{2} = 4.95984a_0 \cos \frac{60.27^\circ}{2} = 4.28952a_0 \quad (15.136)$$

The lengths  $d_1$ ,  $d_2$ , and  $2c'_{S=O}$  define a triangle wherein the angle between  $d_1$  and the internuclear distance between  $O$  and  $S$ ,  $2c'_{S=O}$ , is the dihedral angle  $\theta_{\angle S=O/CSC'}$  that can be solved using the law of cosines (Eq. (15.108)):

$$\begin{aligned} \theta_{\angle S=O/CSC'} &= \cos^{-1} \left( \frac{d_1^2 + (2c'_{S=O})^2 - d_2^2}{2d_1(2c'_{S=O})} \right) \\ &= \cos^{-1} \left( \frac{(2.23423)^2 + (2.81792)^2 - (4.28952)^2}{2(2.23423)(2.81792)} \right) \\ &= 115.74^\circ \end{aligned} \quad (15.137)$$

The experimental [1] dihedral angle  $\theta_{\angle S=O/CSC}$  is

$$\theta_{\angle S=O/CSC} = 115.5^\circ$$

(15.138)

SULFITES ( $C_nH_{2n+2}(SO_3)_m$ ,  $n=2,3,4,5,\dots\infty$ )

The alkyl sulfites,  $C_nH_{2n+2}(SO_3)_m$ , comprise a  $C-O-SO-O-C$  moiety that comprises two types  $C-O$  functional groups, one for methyl and one for alkyl, and  $O-S$  and  $SO$  functional groups. The alkyl portion of the alkyl sulfite may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in sulfites are equivalent to those in branched-chain alkanes.

The  $SO$  functional group is equivalent to that of sulfoxides with  $E_T(atom - atom, msp^3.AO) = 0$  as given in the Sulfoxides section. The methyl and alkyl  $C-O$  functional groups having  $E_T(atom - atom, msp^3.AO) = -1.44915 \text{ eV}$  and  $E_T(atom - atom, msp^3.AO) = -1.65376 \text{ eV}$ , respectively, are equivalent to the corresponding ether groups given in the Ethers section except for the energy terms corresponding to oscillation of the bond in the transition state.

The electron configuration of oxygen is  $1s^2 2s^2 2p^4$ , and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state  $^3P_2$ . The  $SO$  functional group comprises a double bond between the  $S$  atom and the two unpaired electrons of  $O$ . The  $S$  atom also forms single bonds with two additional oxygen atoms that are each further bound to methyl or alkyl groups. The first bond-order bonding in the  $O-S$  groups is between the sulfur atom and a  $O2p$  AO of each oxygen of the two bonds. The formation of these four bonds with the sulfur atom is permitted by the hybridization of the four electrons of the  $S3p$  shell to give the orbital arrangement given by Eq. (15.129). Then, the Coulombic energy  $E_{Coulomb}(S, 3sp^3)$  of the outer electron of the  $S3sp^3$  shell given by Eq. (15.120) with  $r_{3sp^3} = 1.17585a_0$  (Eq. (15.119)) is  $-11.57099 \text{ eV}$ . Using Eq. (15.16) with the radius of the

sulfur atom  $r_{16} = 1.32010a_0$  given by Eq. (10.341), the energy  $E(S3sp^3)$  of the outer electron of the  $S3sp^3$  shell given by the sum of  $E_{Coulomb}(S3sp^3)$  and  $E(magnetic)$  is  $E(S3sp^3) = -11.52126 \text{ eV}$  (Eq. (15.130)).

Thus, the  $O-S$  group is solved as an energy minimum by hybridizing the four  $S3p$  5 electrons to form a  $S3sp^3$  shell, and the sharing of electrons between the  $O2p$  AO and the  $S3sp^3$  HO to form a MO permits each participating orbital to decrease in radius and energy. As in the case of thiols, sulfides, disulfides, and sulfoxides, the energy of sulfur is less than the Coulombic energy between the electron and proton of  $H$  given by Eq. (1.243). Thus,  $c_1$  and  $c_2$  are equal to one in Eq. (15.52), and the energy matching condition is determined by the  $C_2$  10 parameter. Each  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)), and the  $S$  HO has an energy of  $E(S3sp^3) = -11.52126 \text{ eV}$ . To meet the equipotential condition of the union of the  $O-S$   $H_2$ -type-ellipsoidal-MO with these orbitals with the oxygen that further bonds to a  $C2sp^3$  HO, the hybridization factor  $C_2$  of Eq. (15.52) for the  $O-S$ -bond MO given by Eqs. 15 (15.68) and (15.70) is

$$\begin{aligned} C_2(S3sp^3 \text{ to } O \text{ to } C2sp^3 HO) &= \frac{E(S,3sp^3)}{E(O,2p)} c_2(C2sp^3 HO) \\ &= \frac{-11.52126 \text{ eV}}{-13.61806 \text{ eV}} (0.91771) \\ &= 0.77641 \end{aligned} \quad (15.139)$$

As in the case of thiols, sulfides, disulfides, and sulfoxides, with the energy of  $S$  matched to the Coulombic energy between the electron and proton of  $H$ , the energy of the  $O-S$ -bond MO is the sum of the component energies of the  $H_2$ -type ellipsoidal MO given in 20 Eq. (15.42) with  $E(AO/HO) = 0$  and  $E_T(AO/HO) = \Delta E_{H_2MO}(AO/HO)$ . For sulfites,  $\Delta E_{H_2MO}(AO/HO) = -0.92918 \text{ eV}$  and equivalently,  $E_T(atom-atom,msp^3.AO) = -0.92918 \text{ eV}$  (Eq. (14.513)) due to the maximum energy match with the oxygen AO as in the case with carboxylic acid esters.

The symbols of the functional groups of branched-chain alkyl sulfites are given in Table 15.177. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfites are given in Tables 15.178, 15.179, and 15.180, respectively. The total energy of each alkyl sulfite given in Table 5 15.175 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.180 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl sulfites determined using Eqs. (15.79-15.108) are given in Table 15.182.

Table 15.177. The symbols of functional groups of alkyl sulfites.

| Functional Group      | Group Symbol             |
|-----------------------|--------------------------|
| C-O (methyl)          | $C-O$ (i)                |
| C-O (alkyl)           | $C-O$ (ii)               |
| O-SO <sub>2</sub>     | $O-S$                    |
| SO                    | $SO$                     |
| CH <sub>3</sub> group | $C-H$ (CH <sub>3</sub> ) |
| CH <sub>2</sub> group | $C-H$ (CH <sub>2</sub> ) |
| CH                    | $C-H$                    |
| CC bond (n-C)         | $C-C$ (a)                |
| CC bond (iso-C)       | $C-C$ (b)                |
| CC bond (tert-C)      | $C-C$ (c)                |
| CC (iso to iso-C)     | $C-C$ (d)                |
| CC (t to t-C)         | $C-C$ (e)                |
| CC (t to iso-C)       | $C-C$ (f)                |



Table 15.178. The geometrical bond parameters of alkyl sulfites and experimental values [1].

| Parameter                  | C-O (i)<br>Group | C-O (ii)<br>Group | O-S                                        | SO                               | C-H (CH <sub>3</sub> )<br>Group                 | C-H (CH <sub>2</sub> )<br>Group                 | C-H<br>Group         | C-C (a)<br>Group                        | C-C (b)<br>Group                        | C-C (c)<br>Group                        | C-C (d)<br>Group                        | C-C (e)<br>Group                        | C-C (f)<br>Group                        |
|----------------------------|------------------|-------------------|--------------------------------------------|----------------------------------|-------------------------------------------------|-------------------------------------------------|----------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|
| $a$ (Å)                    | 1.80717          | 1.79473           | 1.70299                                    | 1.98517                          | 1.64920                                         | 1.67122                                         | 1.67465              | 2.12499                                 | 2.12499                                 | 2.10725                                 | 2.12499                                 | 2.10725                                 | 2.10725                                 |
| $c'$ (Å)                   | 1.34431          | 1.33968           | 1.48102                                    | 1.40896                          | 1.04856                                         | 1.05553                                         | 1.05661              | 1.45744                                 | 1.45744                                 | 1.45164                                 | 1.45744                                 | 1.45164                                 | 1.45164                                 |
| Bond Length<br>$2c'$ (Å)   | 1.42276          | 1.41785           | 1.56744                                    | 1.49118                          | 1.10974                                         | 1.11713                                         | 1.11827              | 1.54280                                 | 1.54280                                 | 1.53635                                 | 1.54280                                 | 1.53635                                 | 1.53635                                 |
| Exp.<br>Bond Length<br>(Å) |                  |                   | 1.574<br>(H <sub>2</sub> SO <sub>4</sub> ) | 1.485<br>(dimethyl<br>sulfoxide) | 1.107<br>(C-H propane)<br>1.117<br>(C-H butane) | 1.107<br>(C-H propane)<br>1.117<br>(C-H butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $h, c$ (Å)                 | 1.20776          | 1.19429           | 0.84069                                    | 1.39847                          | 1.27295                                         | 1.29569                                         | 1.29924              | 1.54616                                 | 1.54616                                 | 1.52750                                 | 1.54616                                 | 1.52750                                 | 1.52750                                 |
| $e$                        | 0.74388          | 0.74645           | 0.86966                                    | 0.70974                          | 0.63380                                         | 0.63159                                         | 0.63093              | 0.68600                                 | 0.68600                                 | 0.68888                                 | 0.68600                                 | 0.68888                                 | 0.68888                                 |

Table 15.179. The MO to HO intercept geometrical bond parameters of alkyl sulfates.  $R, R', R''$  are H or alkyl groups.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{msp}, \text{AO})$ .

| Bond                                                                                               | Atom           | $E_T$<br>(eV)<br>Bond 1 | $E_T$<br>(eV)<br>Bond 2 | $E_T$<br>(eV)<br>Bond 3 | $E_T$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>C2sp <sup>2</sup><br>(eV) | $r_{\text{final}}$<br>(a <sub>0</sub> ) | $r_{\text{initial}}$<br>(a <sub>0</sub> ) | $E_{\text{orbital}}$<br>(eV)<br>Final | $E(\text{C2sp}^2)$<br>(eV)<br>Final | $\theta^*$<br>(°) | $\theta_1$<br>(°) | $\theta_2$<br>(°) | $d_1$<br>(a <sub>0</sub> ) | $d_2$<br>(a <sub>0</sub> ) |
|----------------------------------------------------------------------------------------------------|----------------|-------------------------|-------------------------|-------------------------|-------------------------|----------------------------------------------------|-----------------------------------------|-------------------------------------------|---------------------------------------|-------------------------------------|-------------------|-------------------|-------------------|----------------------------|----------------------------|
| $(\text{RO})_2\text{S}=\text{O}_a$                                                                 | S              | 0                       | -0.46459                | -0.46459                | 0                       |                                                    | 1.32010                                 | 0.86359                                   | -15.75493                             |                                     | 78.56             | 101.44            | 37.25             | 1.58026                    | 0.17130                    |
| $(\text{RO})_2\text{S}=\text{O}_a$                                                                 | O <sub>a</sub> | 0                       | 0                       | 0                       | 0                       |                                                    | 1.00000                                 | 0.91771                                   | -14.82375                             |                                     | 84.06             | 95.94             | 40.75             | 1.50400                    | 0.09304                    |
| $\text{CH}_3\text{O}_a-\text{S}(\text{O})\text{OR}^*$                                              | S              | -0.46459                | -0.46459                | 0                       | 0                       |                                                    | 1.32010                                 | 0.86359                                   | -15.75493                             |                                     | 126.68            | 53.32             | 55.47             | 0.96321                    | 0.51381                    |
| $\text{CH}_3\text{O}_a-\text{S}(\text{O})\text{OR}^*$                                              | O <sub>a</sub> | -0.46459                | -0.72457                | 0                       | 0                       |                                                    | 1.00000                                 | 0.84957                                   | -16.01492                             |                                     | 126.03            | 53.97             | 54.81             | 0.98133                    | 0.49959                    |
| $\text{RC}(\text{H})\text{O}_a-\text{S}(\text{O})\text{OR}^*$                                      | O <sub>a</sub> | -0.46459                | -0.82688                | 0                       | 0                       |                                                    | 1.00000                                 | 0.84418                                   | -16.11722                             |                                     | 125.77            | 54.23             | 54.56             | 0.98753                    | 0.49499                    |
| $\text{H}_3\text{C}_a-\text{O}_a\text{S}(\text{O})\text{OR}^*$                                     | O <sub>a</sub> | -0.72457                | -0.46459                | 0                       | 0                       |                                                    | 1.00000                                 | 0.84957                                   | -16.01492                             |                                     | 93.85             | 86.15             | 44.57             | 1.28731                    | 0.05700                    |
| $\text{H}_3\text{C}_a-\text{O}_a\text{S}(\text{O})\text{OR}^*$                                     | C <sub>a</sub> | -0.72457                | 0                       | 0                       | 0                       | -152.34036                                         | 0.91771                                 | 0.87495                                   | -15.55033                             | -15.39946                           | 95.98             | 84.02             | 46.10             | 1.25319                    | 0.09112                    |
| $\text{RH}_2\text{C}_a-\text{O}_a\text{S}(\text{O})\text{OR}^*$                                    | O <sub>a</sub> | -0.82688                | -0.46459                | 0                       | 0                       |                                                    | 1.00000                                 | 0.84418                                   | -16.11722                             |                                     | 94.50             | 85.50             | 44.80             | 1.27343                    | 0.06624                    |
| $\text{RH}_2\text{C}_a-\text{O}_a\text{S}(\text{O})\text{OR}^*$                                    | C <sub>a</sub> | -0.82688                | -0.92918                | 0                       | 0                       | -153.37175                                         | 0.91771                                 | 0.82053                                   | -16.38181                             | -16.39093                           | 92.41             | 87.59             | 43.35             | 1.30512                    | 0.03456                    |
| $\text{C}^*-H(\text{C}^*)$                                                                         | C              | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                         | 0.91771                                 | 0.86359                                   | -15.75493                             | -15.56407                           | 77.49             | 102.51            | 41.48             | 1.23564                    | 0.18708                    |
| $\text{C}^*-H(\text{C}^*)$                                                                         | C              | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                         | 0.91771                                 | 0.81549                                   | -16.68412                             | -16.49325                           | 68.47             | 111.53            | 35.84             | 1.35486                    | 0.29933                    |
| $\text{C}^*-H(\text{C}^*)$                                                                         | C              | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                         | 0.91771                                 | 0.77247                                   | -17.61330                             | -17.42344                           | 61.10             | 118.90            | 31.37             | 1.42988                    | 0.37236                    |
| $\text{H}_3\text{C}_a\text{H}_2\text{C}_a\text{H}_2-\text{C}^*(\text{C}^*)$                        | C <sub>a</sub> | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                         | 0.91771                                 | 0.86359                                   | -15.75493                             | -15.56407                           | 63.82             | 116.18            | 30.08             | 1.83879                    | 0.38106                    |
| $\text{H}_3\text{C}_a\text{H}_2\text{C}_a\text{H}_2-\text{C}^*(\text{C}^*)$                        | C <sub>a</sub> | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                         | 0.91771                                 | 0.81549                                   | -16.68412                             | -16.49325                           | 56.41             | 123.59            | 26.06             | 1.90890                    | 0.45117                    |
| $\text{R}-\text{H}_2\text{C}_a(\text{H}_2\text{C}_a-\text{R}')\text{HCH}_2-\text{C}^*(\text{C}^*)$ | C <sub>a</sub> | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                         | 0.91771                                 | 0.77247                                   | -17.61330                             | -17.42344                           | 48.30             | 131.70            | 21.90             | 1.97162                    | 0.51388                    |
| $\text{R}-\text{H}_2\text{C}_a(\text{H}_2\text{C}_a-\text{R}')\text{HCH}_2-\text{C}^*(\text{C}^*)$ | C <sub>a</sub> | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -154.71860                                         | 0.91771                                 | 0.73889                                   | -17.92866                             | -17.73779                           | 48.21             | 131.79            | 21.74             | 1.95734                    | 0.50570                    |
| $\text{R}-\text{H}_2\text{C}_a(\text{H}_2\text{C}_a-\text{R}')\text{HCH}_2-\text{C}^*(\text{C}^*)$ | C <sub>a</sub> | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                         | 0.91771                                 | 0.77247                                   | -17.61330                             | -17.42344                           | 48.30             | 131.70            | 21.90             | 1.97162                    | 0.51388                    |
| $\text{R}-\text{H}_2\text{C}_a(\text{H}_2\text{C}_a-\text{R}')\text{HCH}_2-\text{C}^*(\text{C}^*)$ | C <sub>a</sub> | -0.92918                | -0.92918                | -0.92918                | -0.72457                | -154.51399                                         | 0.91771                                 | 0.76765                                   | -17.92866                             | -17.73779                           | 50.04             | 129.96            | 22.66             | 1.94462                    | 0.49298                    |
| $\text{R}-\text{H}_2\text{C}_a(\text{H}_2\text{C}_a-\text{R}')\text{HCH}_2-\text{C}^*(\text{C}^*)$ | C <sub>a</sub> | -0.72457                | -0.92918                | -0.92918                | 0                       | -154.19863                                         | 0.91771                                 | 0.78155                                   | -17.40869                             | -17.21783                           | 52.78             | 127.22            | 24.04             | 1.93443                    | 0.47279                    |
| $\text{R}-\text{H}_2\text{C}_a(\text{H}_2\text{C}_a-\text{R}')\text{HCH}_2-\text{C}^*(\text{C}^*)$ | C <sub>a</sub> | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.51399                                         | 0.91771                                 | 0.76765                                   | -17.92866                             | -17.73779                           | 50.04             | 129.96            | 22.66             | 1.94462                    | 0.49298                    |

Table 15.180. The energy parameters (eV) of functional groups of allyl sulfites.

| Parameters                        | C-O (i)   | C-O (ii)  | O-S       | SO        | CH <sub>3</sub> | CH <sub>2</sub> | C-H       | C-C (a)   | C-C (b)   | C-C (c)   | C-C (d)   | C-C (e)   | C-C (f)   |
|-----------------------------------|-----------|-----------|-----------|-----------|-----------------|-----------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| $\eta_1$                          | 1         | 1         | 1         | 2         | 2               | 2               | 1         | 1         | 1         | 1         | 1         | 1         | 1         |
| $\eta_2$                          | 0         | 0         | 0         | 0         | 1               | 1               | 0         | 0         | 0         | 0         | 0         | 0         | 0         |
| $\eta_3$                          | 0         | 0         | 0         | 0         | 0               | 0               | 0         | 0         | 0         | 0         | 0         | 0         | 0         |
| $\zeta_1$                         | 0.5       | 0.5       | 0.5       | 0.5       | 0.75            | 0.75            | 0.75      | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       |
| $\zeta_2$                         | 1         | 1         | 0.77641   | 1         | 1               | 1               | 1         | 1         | 1         | 1         | 1         | 1         | 1         |
| $\zeta_3$                         | 1         | 1         | 1         | 1         | 1               | 1               | 1         | 1         | 1         | 1         | 1         | 1         | 1         |
| $\zeta_4$                         | 0.85395   | 0.85395   | 1         | 1.20632   | 0.91771         | 0.91771         | 0.91771   | 0.91771   | 0.91771   | 0.91771   | 0.91771   | 0.91771   | 0.91771   |
| $\zeta_5$                         | 0         | 0         | 0         | 0         | 0               | 1               | 1         | 0         | 0         | 0         | 1         | 1         | 0         |
| $\zeta_6$                         | 2         | 2         | 2         | 4         | 1               | 1               | 1         | 2         | 2         | 2         | 2         | 2         | 2         |
| $\zeta_7$                         | 0         | 0         | 0         | 1         | 3               | 2               | 1         | 0         | 0         | 0         | 0         | 0         | 0         |
| $\zeta_8$                         | 0.5       | 0.5       | 0.5       | 0.5       | 0.75            | 0.75            | 0.75      | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       |
| $\zeta_9$                         | 1         | 1         | 0.77641   | 1         | 1               | 1               | 1         | 1         | 1         | 1         | 1         | 1         | 1         |
| $\zeta_{10}$                      | -33.15757 | -33.47304 | -48.95512 | -82.65003 | -107.32728      | -70.41425       | -35.12015 | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $V_1$ (eV)                        | 10.12103  | 10.15605  | 9.18680   | 19.31325  | 38.92728        | 25.78002        | 12.87680  | 9.33552   | 9.33552   | 9.37273   | 9.33552   | 9.37273   | 9.37273   |
| $T$ (eV)                          | 9.17389   | 9.32537   | 14.36741  | 20.81183  | 32.53914        | 21.06675        | 10.48582  | 6.77464   | 6.77464   | 6.90500   | 6.77464   | 6.90500   | 6.90500   |
| $V_{\text{an}}$ (eV)              | -4.58695  | -4.66268  | -7.18371  | -10.40592 | -16.26957       | -10.53337       | -5.24291  | -3.38732  | -3.38732  | -3.45250  | -3.38732  | -3.45250  | -3.45250  |
| $E_{\text{an}}$ (eV)              | -14.63489 | -14.63489 | 0         | -11.52126 | -15.56407       | -15.56407       | -14.63489 | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 |
| $\Delta E_{\text{an}}$ (eV)       | -1.44915  | -1.65376  | -0.92918  | -1.16125  | 0               | 0               | 0         | 0         | 0         | 0         | 0         | 0         | 0         |
| $E_{\text{an}}$ (eV)              | -13.18574 | -12.98113 | 0.92918   | -10.56001 | -15.56407       | -15.56407       | -14.63489 | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 |
| $E_{\text{an}}$ (eV)              | -31.63533 | -31.63544 | -31.63543 | -63.27088 | -67.69451       | -49.66493       | -31.63533 | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_{\text{an}}$ (eV)              | -1.44915  | -1.65376  | -0.92918  | 0         | 0               | 0               | 0         | -1.83836  | -1.83836  | -1.44915  | -1.83836  | -1.44915  | -1.44915  |
| $E_{\text{an}}$ (eV)              | -33.08452 | -33.28912 | -32.56455 | -63.27074 | -67.69450       | -49.66493       | -31.63537 | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega$ (10 <sup>15</sup> rad/s) | 22.0240   | 12.1583   | 33.4164   | 17.6762   | 24.9286         | 24.2751         | 24.1759   | 9.43699   | 9.43699   | 15.4846   | 9.43699   | 9.55643   | 9.55643   |
| $E_{\text{an}}$ (eV)              | 14.49660  | 8.00277   | 21.99527  | 11.63476  | 16.40846        | 15.97831        | 15.91299  | 6.21159   | 6.21159   | 10.19220  | 6.21159   | 6.29021   | 6.29021   |
| $E_{\text{an}}$ (eV)              | -0.24921  | -0.18631  | -0.30214  | -0.21348  | -0.25532        | -0.25017        | -0.24966  | -0.16515  | -0.16515  | -0.20896  | -0.16515  | -0.16416  | -0.16416  |
| $E_{\text{an}}$ (eV)              | 0.13663   | 0.13663   | 0.08679   | 0.12832   | 0.35532         | 0.35532         | 0.35532   | 0.12312   | 0.12312   | 0.09944   | 0.12312   | 0.12312   | 0.12312   |
| $E_{\text{an}}$ (eV)              | 12.11     | 12.11     | 14.21     | 14.31     | 14.31           | 14.31           | 14.31     | 14.31     | 14.31     | 14.31     | 14.31     | 14.31     | 14.31     |
| $E_{\text{an}}$ (eV)              | -0.18089  | -0.11799  | -0.22875  | -0.14952  | -0.22757        | -0.14502        | -0.07200  | -0.10359  | -0.07526  | -0.15924  | -0.10359  | -0.10260  | -0.10260  |
| $E_{\text{an}}$ (eV)              | 0.14803   | 0.14803   | 0.11441   | 0.11441   | 0.14803         | 0.14803         | 0.14803   | 0.14803   | 0.14803   | 0.14803   | 0.14803   | 0.14803   | 0.14803   |
| $E_{\text{an}}$ (eV)              | -33.26541 | -33.40711 | -32.82530 | -63.56937 | -67.92207       | -49.80996       | -31.70737 | -33.59732 | -33.59732 | -33.26541 | -33.59732 | -33.18712 | -33.18712 |
| $E_{\text{an}}$ (eV)              | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489       | -14.63489       | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{\text{an}}$ (eV)              | 0         | 0         | 0         | -1.16125  | -13.59844       | -13.59844       | -13.59844 | 0         | 0         | 0         | 0         | 0         | 0         |
| $E_{\text{an}}$ (eV)              | 3.99563   | 4.13733   | 3.55352   | 3.68556   | 12.49186        | 7.85016         | 3.36601   | 4.32754   | 4.29921   | 3.97598   | 4.17951   | 3.62128   | 3.91734   |

Table 15.181. The total bond energies of allyl sulfites calculated using the functional group composition and the energies of Table 15.180 compared to the experimental values [3].

| Formula                         | C-O (i) | C-O (ii) | O-S | SO | CH <sub>3</sub> | CH <sub>2</sub> | C-H | C-C (a) | C-C (b) | C-C (c) | C-C (d) | C-C (e) | C-C (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---------------------------------|---------|----------|-----|----|-----------------|-----------------|-----|---------|---------|---------|---------|---------|---------|-----------------------------------|-------------------------------------|----------------|
| CH <sub>3</sub> SO <sub>2</sub> | 2       | 0        | 2   | 1  | 2               | 0               | 0   | 0       | 0       | 0       | 0       | 0       | 0       | 45.95038                          | 44.642                              | 0.0207         |
| CH <sub>3</sub> SO <sub>2</sub> | 0       | 2        | 2   | 1  | 2               | 2               | 2   | 0       | 0       | 0       | 0       | 0       | 0       | 68.54939                          | 68.648                              | 0.00143        |
| CH <sub>3</sub> SO <sub>2</sub> | 0       | 2        | 2   | 1  | 2               | 6               | 6   | 0       | 0       | 0       | 0       | 0       | 0       | 117.18019                         | 117.191                             | 0.00069        |



# SULFATES ( $C_nH_{2n+2}(SO_4)_m$ , $n=2,3,4,5,\dots,\infty$ )

The alkyl sulfates,  $C_nH_{2n+2}(SO_4)_m$ , comprise a  $C-O-SO_2-O-C$  moiety that comprises two types  $C-O$  functional groups, one for methyl and one for alkyl, and  $O-S$  and  $SO_2$  functional groups. The alkyl portion of the alkyl sulfate may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in sulfates are equivalent to those in branched-chain alkanes.

The methyl and alkyl  $C-O$  functional groups having  $E_r(atom-atom,msp^3.AO)=-1.44915\text{ eV}$  and  $E_r(atom-atom,msp^3.AO)=-1.65376\text{ eV}$ , respectively, are equivalent to the corresponding groups given in the Sulfites section. The  $O-S$  functional group having  $E_r(atom-atom,msp^3.AO)=-0.92918\text{ eV}$  is equivalent to that given in the Sulfites section. The  $SO_2$  functional group is equivalent to that of sulfones with  $E_r(atom-atom,msp^3.AO)=0$  as given in the Sulfones section.

The symbols of the functional groups of branched-chain alkyl sulfates are given in Table 15.183. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfates are given in Tables 15.184, 15.185, and 15.186, respectively. The total energy of each alkyl sulfate given in Table 15.187 was calculated as the sum over the integer multiple of each  $E_p(group)$  of Table 15.186 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl sulfates determined using Eqs. (15.79-15.108) are given in Table 15.188.

Table 15.183. The symbols of functional groups of alkyl sulfates.

| Functional Group      | Group Symbol           |
|-----------------------|------------------------|
| C-O (methyl)          | C-O (i)                |
| C-O (alkyl)           | C-O (ii)               |
| O-SO <sub>2</sub>     | O-S                    |
| SO <sub>2</sub>       | SO <sub>2</sub>        |
| CH <sub>3</sub> group | C-H (CH <sub>3</sub> ) |
| CH <sub>2</sub> group | C-H (CH <sub>2</sub> ) |
| CH                    | C-H                    |
| CC bond (n-C)         | C-C' (a)               |
| CC bond (iso-C)       | C-C' (b)               |
| CC bond (tert-C)      | C-C' (c)               |
| CC (iso to iso-C)     | C-C' (d)               |
| CC (t to t-C)         | C-C' (e)               |
| CC (t to iso-C)       | C-C' (f)               |

Table 15.184. The geometrical bond parameters of alkyl sulfates and experimental values [1].

| Parameter            | C-O (i)<br>Group | C-O (ii)<br>Group | O-S                                        | SO <sub>2</sub>             | C-H (CH <sub>3</sub> )<br>Group                 | C-H<br>Group         | C-C (a)<br>Group                        | C-C (b)<br>Group                        | C-C (c)<br>Group                        | C-C (d)<br>Group                        | C-C (e)<br>Group                        | C-C (f)<br>Group                        |
|----------------------|------------------|-------------------|--------------------------------------------|-----------------------------|-------------------------------------------------|----------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|
| $a$ (Å)              | 1.80717          | 1.79473           | 1.70299                                    | 1.83851                     | 1.67122                                         | 1.67465              | 2.12499                                 | 2.12499                                 | 2.10725                                 | 2.12499                                 | 2.10725                                 | 2.10725                                 |
| $c'$ (Å)             | 1.34451          | 1.33968           | 1.48102                                    | 1.36327                     | 1.05553                                         | 1.05661              | 1.45744                                 | 1.45744                                 | 1.45164                                 | 1.45744                                 | 1.45164                                 | 1.45164                                 |
| Bond Length          | 1.42276          | 1.41785           | 1.56744                                    | 1.44282                     | 1.11713                                         | 1.11827              | 1.54280                                 | 1.54280                                 | 1.53635                                 | 1.54280                                 | 1.53635                                 | 1.53635                                 |
| $2c'$ (Å)            |                  |                   |                                            |                             |                                                 |                      |                                         |                                         |                                         |                                         |                                         |                                         |
| Exp. Bond Length (Å) |                  |                   | 1.574<br>(H <sub>2</sub> SO <sub>4</sub> ) | 1.435<br>(dimethyl sulfone) | 1.107<br>(C-H propane)<br>1.117<br>(C-H butane) | 1.122<br>(isobutane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $h, c'$ (Å)          | 1.20776          | 1.19429           | 0.84069                                    | 1.26315                     | 1.29569                                         | 1.29924              | 1.54616                                 | 1.54616                                 | 1.52750                                 | 1.54616                                 | 1.52750                                 | 1.52750                                 |
| $e'$                 | 0.74388          | 0.74645           | 0.86966                                    | 0.73353                     | 0.63159                                         | 0.63095              | 0.68600                                 | 0.68600                                 | 0.68888                                 | 0.68600                                 | 0.68888                                 | 0.68888                                 |

Table 15.185. The MO to HO intercept geometrical bond parameters of alkyl sulfates.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{msp}^2, \text{AO})$ .

| Bond                                                                                                                   | Atom           | $E_T$<br>(eV)<br>Bond 1 | $E_T$<br>(eV)<br>Bond 2 | $E_T$<br>(eV)<br>Bond 3 | $E_T$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>C2sp <sup>2</sup><br>(eV) | $r_{\text{final}}$<br>(a <sub>0</sub> ) | $r_{\text{final}}$<br>(a <sub>0</sub> ) | $E_{\text{Final}}$<br>(eV)<br>Final | $E(\text{C2sp}^2)$<br>(eV)<br>Final | $\theta^*$<br>(°) | $\theta_1$<br>(°) | $\theta_2$<br>(°) | $d_1$<br>(a <sub>0</sub> ) | $d_2$<br>(a <sub>0</sub> ) |
|------------------------------------------------------------------------------------------------------------------------|----------------|-------------------------|-------------------------|-------------------------|-------------------------|----------------------------------------------------|-----------------------------------------|-----------------------------------------|-------------------------------------|-------------------------------------|-------------------|-------------------|-------------------|----------------------------|----------------------------|
| $(\text{RO})_2(\text{O}_2)\text{S}=\text{O}_s$                                                                         | S              | 0                       | 0                       | -0.46459                | -0.46459                |                                                    | 1.32010                                 | 0.86359                                 | -15.75493                           |                                     | 90.46             | 89.54             | 43.13             | 1.35635                    | 0.00693                    |
| $(\text{RO})_2(\text{O}_2)\text{S}=\text{O}_s$                                                                         | O <sub>s</sub> | 0                       | 0                       | 0                       | 0                       |                                                    | 1.00000                                 | 0.91771                                 | -14.82575                           |                                     | 95.05             | 84.95             | 46.36             | 1.28256                    | 0.08071                    |
| $\text{CH}_3\text{O}_2-\text{S}(\text{O}_2)\text{OR}^*$                                                                | S              | -0.46459                | -0.46459                | 0                       | 0                       |                                                    | 1.32010                                 | 0.86359                                 | -15.75493                           |                                     | 126.68            | 53.32             | 55.47             | 0.96521                    | 0.51581                    |
| $\text{CH}_3\text{O}_2-\text{S}(\text{O}_2)\text{OR}^*$                                                                | O <sub>s</sub> | -0.46459                | -0.72457                | 0                       | 0                       |                                                    | 1.00000                                 | 0.84957                                 | -16.01492                           |                                     | 126.03            | 53.97             | 54.81             | 0.98133                    | 0.49569                    |
| $(\text{C}-\text{O}(\text{ii}))$                                                                                       | O <sub>s</sub> | -0.46459                | -0.82688                | 0                       | 0                       |                                                    | 1.00000                                 | 0.84418                                 | -16.11722                           |                                     | 125.77            | 54.23             | 54.56             | 0.98753                    | 0.49349                    |
| $\text{RCH}_2\text{O}_2-\text{S}(\text{O}_2)\text{OR}^*$                                                               | O <sub>s</sub> | -0.46459                | -0.82688                | 0                       | 0                       |                                                    | 1.00000                                 | 0.84957                                 | -16.01492                           |                                     | 93.85             | 86.15             | 44.57             | 1.28731                    | 0.05700                    |
| $\text{H}_3\text{C}_s-\text{O}_2\text{S}(\text{O}_2)\text{OR}$                                                         | O <sub>s</sub> | -0.72457                | -0.46459                | 0                       | 0                       |                                                    | 1.00000                                 | 0.84957                                 | -16.01492                           |                                     | 93.85             | 86.15             | 44.57             | 1.28731                    | 0.05700                    |
| $\text{H}_3\text{C}_s-\text{O}_2\text{S}(\text{O}_2)\text{OR}$                                                         | C <sub>s</sub> | -0.72457                | 0                       | 0                       | 0                       | -152.34026                                         | 0.91771                                 | 0.87495                                 | -15.53033                           | -15.35946                           | 95.98             | 84.02             | 46.10             | 1.25319                    | 0.09112                    |
| $\text{RH}_2\text{C}_s-\text{O}_2\text{S}(\text{O}_2)\text{OR}^*$                                                      | O <sub>s</sub> | -0.82688                | -0.46459                | 0                       | 0                       |                                                    | 1.00000                                 | 0.84418                                 | -16.11722                           |                                     | 94.30             | 85.50             | 44.80             | 1.27343                    | 0.06624                    |
| $\text{RH}_2\text{C}_s-\text{O}_2\text{S}(\text{O}_2)\text{OR}^*$                                                      | C <sub>s</sub> | -0.82688                | -0.92918                | 0                       | 0                       | -153.37175                                         | 0.91771                                 | 0.82053                                 | -16.58181                           | -16.35095                           | 92.41             | 87.59             | 43.35             | 1.30512                    | 0.03456                    |
| $(\text{C}-\text{O}(\text{iii}))$                                                                                      | C <sub>s</sub> | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                         | 0.91771                                 | 0.86359                                 | -15.75493                           | -15.56407                           | 77.49             | 102.51            | 41.48             | 1.23564                    | 0.18708                    |
| $\text{C}-\text{H}(\text{CH}_3)$                                                                                       | C <sub>s</sub> | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                         | 0.91771                                 | 0.81549                                 | -16.68412                           | -16.49325                           | 68.47             | 111.53            | 35.84             | 1.35486                    | 0.29933                    |
| $\text{C}-\text{H}(\text{CH}_3)$                                                                                       | C <sub>s</sub> | -0.92918                | -0.92918                | 0                       | 0                       | -154.40324                                         | 0.91771                                 | 0.77247                                 | -17.61330                           | -17.42244                           | 61.10             | 118.90            | 31.37             | 1.42988                    | 0.37326                    |
| $\text{C}-\text{H}(\text{CH})$                                                                                         | C <sub>s</sub> | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                         | 0.91771                                 | 0.86359                                 | -15.75493                           | -15.56407                           | 63.82             | 116.18            | 30.08             | 1.83579                    | 0.38106                    |
| $\text{H}_3\text{C}_s\text{C}_s\text{H}_2\text{CH}_2-$                                                                 | C <sub>s</sub> | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                         | 0.91771                                 | 0.81549                                 | -16.68412                           | -16.49325                           | 56.41             | 123.59            | 26.06             | 1.90890                    | 0.45117                    |
| $\text{H}_3\text{C}_s\text{C}_s\text{H}_2\text{CH}_2-$                                                                 | C <sub>s</sub> | -0.92918                | -0.92918                | 0                       | 0                       | -154.40324                                         | 0.91771                                 | 0.77247                                 | -17.61330                           | -17.42244                           | 48.30             | 131.70            | 21.90             | 1.97162                    | 0.51388                    |
| $\text{R}-\text{H}_2\text{C}_s\text{C}_s(\text{H}_2\text{C}_s-\text{R}')\text{HCH}_2-$                                 | C <sub>s</sub> | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                         | 0.91771                                 | 0.77247                                 | -17.61330                           | -17.42244                           | 48.30             | 131.70            | 21.90             | 1.97162                    | 0.51388                    |
| $(\text{C}-\text{C}(\text{bi}))$                                                                                       | C <sub>s</sub> | -0.92918                | -0.92918                | -0.92918                | -0.72457                | -154.71860                                         | 0.91771                                 | 0.75889                                 | -17.92866                           | -17.73779                           | 48.21             | 131.79            | 21.74             | 1.95734                    | 0.50570                    |
| $\text{R}-\text{H}_2\text{C}_s(\text{R}'-\text{H}_2\text{C}_s)\text{C}_s(\text{R}''-\text{H}_2\text{C}_s)\text{CH}_2-$ | C <sub>s</sub> | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -154.71860                                         | 0.91771                                 | 0.75889                                 | -17.92866                           | -17.73779                           | 48.21             | 131.79            | 21.74             | 1.95734                    | 0.50570                    |
| $(\text{C}-\text{C}(\text{e}))$                                                                                        | C <sub>s</sub> | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                         | 0.91771                                 | 0.77247                                 | -17.61330                           | -17.42244                           | 48.30             | 131.70            | 21.90             | 1.97162                    | 0.51388                    |
| $\text{RCH}_2\text{C}_s\text{C}_s(\text{H}_2\text{C}_s-\text{R}')\text{HCH}_2-$                                        | C <sub>s</sub> | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                         | 0.91771                                 | 0.77247                                 | -17.61330                           | -17.42244                           | 48.30             | 131.70            | 21.90             | 1.97162                    | 0.51388                    |
| $(\text{C}-\text{C}(\text{di}))$                                                                                       | C <sub>s</sub> | -0.92918                | -0.92918                | -0.92918                | -0.72457                | -154.51399                                         | 0.91771                                 | 0.76765                                 | -17.92866                           | -17.73779                           | 50.04             | 129.96            | 22.66             | 1.94462                    | 0.49298                    |
| $\text{RCH}_2\text{C}_s(\text{R}'-\text{H}_2\text{C}_s)\text{C}_s(\text{R}''-\text{H}_2\text{C}_s)\text{CH}_2-$        | C <sub>s</sub> | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -154.51399                                         | 0.91771                                 | 0.76765                                 | -17.92866                           | -17.73779                           | 50.04             | 129.96            | 22.66             | 1.94462                    | 0.49298                    |
| $(\text{C}-\text{C}(\text{fi}))$                                                                                       | C <sub>s</sub> | -0.72457                | -0.92918                | -0.92918                | 0                       | -154.19863                                         | 0.91771                                 | 0.78155                                 | -17.40869                           | -17.21783                           | 52.78             | 127.22            | 24.04             | 1.92443                    | 0.47279                    |
| $\text{RCH}_2\text{C}_s(\text{R}'-\text{H}_2\text{C}_s)\text{C}_s(\text{R}''-\text{H}_2\text{C}_s)\text{CH}_2-$        | C <sub>s</sub> | -0.72457                | -0.92918                | -0.92918                | -0.72457                | -154.19863                                         | 0.91771                                 | 0.78155                                 | -17.40869                           | -17.21783                           | 52.78             | 127.22            | 24.04             | 1.92443                    | 0.47279                    |
| $(\text{C}-\text{C}(\text{ti}))$                                                                                       | C <sub>s</sub> | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.51399                                         | 0.91771                                 | 0.76765                                 | -17.92866                           | -17.73779                           | 50.04             | 129.96            | 22.66             | 1.94462                    | 0.49298                    |

Table 15.186. The energy parameters (eV) of functional groups of alkyl sulfates.

| Parameters                                       | C-O (i)<br>Group | C-O (ii)<br>Group | O-S<br>Group | SO <sub>2</sub><br>Group | CH <sub>3</sub><br>Group | CH <sub>2</sub><br>Group | C-H<br>Group   | C-C (a)<br>Group | C-C (b)<br>Group | C-C (c)<br>Group | C-C (d)<br>Group | C-C (e)<br>Group | C-C (f)<br>Group |
|--------------------------------------------------|------------------|-------------------|--------------|--------------------------|--------------------------|--------------------------|----------------|------------------|------------------|------------------|------------------|------------------|------------------|
| $n_1$                                            | 1                | 1                 | 1            | 4                        | 3                        | 2                        | 1              | 1                | 1                | 1                | 1                | 1                | 1                |
| $n_2$                                            | 0                | 0                 | 0            | 0                        | 2                        | 1                        | 0              | 0                | 0                | 0                | 0                | 0                | 0                |
| $n_3$                                            | 0                | 0                 | 0            | 0                        | 0                        | 0                        | 0              | 0                | 0                | 0                | 0                | 0                | 0                |
| $C_1$                                            | 0.5              | 0.5               | 0.5          | 0.5                      | 0.75                     | 0.75                     | 0.75           | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              |
| $C_2$                                            | 1                | 1                 | 0.77641      | 1                        | 1                        | 1                        | 1              | 1                | 1                | 1                | 1                | 1                | 1                |
| $C_3$                                            | 1                | 1                 | 1            | 1                        | 1                        | 1                        | 1              | 1                | 1                | 1                | 1                | 1                | 1                |
| $C_4$                                            | 0.85395          | 0.85395           | 1            | 1.20632                  | 0.91771                  | 0.91771                  | 0.91771        | 0.91771          | 0.91771          | 0.91771          | 0.91771          | 0.91771          | 0.91771          |
| $C_5$                                            | 0                | 0                 | 0            | 1                        | 0                        | 1                        | 1              | 0                | 0                | 0                | 1                | 1                | 0                |
| $C_6$                                            | 2                | 2                 | 2            | 8                        | 1                        | 1                        | 1              | 2                | 2                | 2                | 2                | 2                | 2                |
| $C_7$                                            | 0                | 0                 | 0            | 1                        | 3                        | 2                        | 1              | 0                | 0                | 0                | 0                | 0                | 0                |
| $C_{10}$                                         | 0.5              | 0.5               | 0.5          | 0.5                      | 0.75                     | 0.75                     | 0.75           | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              | 0.5              |
| $C_{11}$                                         | 1                | 1                 | 0.77641      | 1                        | 1                        | 1                        | 1              | 1                | 1                | 1                | 1                | 1                | 1                |
| $V_p$ (eV)                                       | -33.15757        | -33.47304         | -48.93512    | -180.36454               | -107.32728               | -70.41425                | -35.12015      | -28.79214        | -28.79214        | -29.10112        | -28.79214        | -29.10112        | -29.10112        |
| $V_r$ (eV)                                       | 10.12103         | 10.15605          | 9.18680      | 39.92103                 | 38.92728                 | 25.78002                 | 12.87680       | 9.33352          | 9.33352          | 9.37273          | 9.33352          | 9.37273          | 9.37273          |
| $T$ (eV)                                         | 9.17389          | 9.32537           | 14.36741     | 48.52397                 | 32.53914                 | 21.06675                 | 10.48582       | 6.77464          | 6.77464          | 6.90500          | 6.77464          | 6.90500          | 6.90500          |
| $V_a$ (eV)                                       | -4.58695         | -4.66268          | -7.18371     | -24.26198                | -16.26957                | -10.53337                | -5.24291       | -3.38732         | -3.38732         | -3.45250         | -3.38732         | -3.45250         | -3.45250         |
| $E_{(10^6 \text{ rad})}$ (eV)                    | -14.63489        | -14.63489         | 0            | -11.52126                | -15.56407                | -15.56407                | -14.63489      | -15.56407        | -15.56407        | -15.55946        | -15.56407        | -15.55946        | -15.55946        |
| $\Delta E_{10^6 \text{ rad}}^{\text{atom}} (eV)$ | -1.44915         | -1.65376          | -0.92918     | -1.16125                 | 0                        | 0                        | 0              | 0                | 0                | 0                | 0                | 0                | 0                |
| $E_{10^6 \text{ rad}}^{\text{atom}} (eV)$        | -13.18574        | -12.98113         | 0.92918      | -10.36001                | -15.56407                | -15.56407                | -14.63489      | -15.56407        | -15.56407        | -15.55946        | -15.56407        | -15.55946        | -15.55946        |
| $E_{10^6 \text{ rad}}^{\text{atom}} (eV)$        | -31.63533        | -31.63544         | -31.63543    | -126.54154               | -67.69451                | -49.66493                | -31.63533      | -31.63537        | -31.63537        | -31.63535        | -31.63537        | -31.63535        | -31.63535        |
| $E_{10^6 \text{ rad}}^{\text{atom}} (eV)$        | -1.44915         | -1.65376          | -0.92918     | 0                        | 0                        | 0                        | 0              | -1.85836         | -1.85836         | -1.44915         | -1.85836         | -1.44915         | -1.44915         |
| $E_{10^6 \text{ rad}}^{\text{atom}} (eV)$        | -33.08452        | -33.28912         | -32.56455    | -126.54147               | -67.69450                | -49.66493                | -31.63537      | -33.40373        | -33.40373        | -33.08452        | -33.40373        | -33.08452        | -33.08452        |
| $\omega (10^6 \text{ rad/s})$                    | 22.0240          | 12.1583           | 33.4164      | 11.5378                  | 24.9286                  | 24.2751                  | 24.1759        | 9.43699          | 9.43699          | 15.4846          | 9.43699          | 15.4846          | 9.55643          |
| $E_{10^6 \text{ rad}}^{\text{atom}} (eV)$        | 14.49660         | 8.00277           | 21.99527     | 7.59437                  | 16.40846                 | 15.97831                 | 15.91299       | 6.21159          | 6.21159          | 10.19220         | 6.21159          | 10.19220         | 6.29021          |
| $E_{10^6 \text{ rad}}^{\text{atom}} (eV)$        | -0.24921         | -0.18631          | -0.30214     | -0.17247                 | -0.23532                 | -0.25017                 | -0.24966       | -0.16515         | -0.16515         | -0.20896         | -0.16515         | -0.16416         | -0.16416         |
| $E_{10^6 \text{ rad}}^{\text{atom}} (eV)$        | 0.13663          | 0.13663           | 0.08679      | 0.12832                  | 0.35532                  | 0.35532                  | 0.35532        | 0.12312          | 0.12312          | 0.09944          | 0.12312          | 0.12312          | 0.12312          |
| $E_{10^6 \text{ rad}}^{\text{atom}} (eV)$        | [21]             | [21]              | [42]         | [43]                     | (Eq. (13.458))           | (Eq. (13.458))           | (Eq. (13.458)) | [2]              | [4]              | [5]              | [2]              | [2]              | [2]              |
| $E_{10^6 \text{ rad}}^{\text{atom}} (eV)$        | -0.18089         | -0.11799          | -0.25875     | -0.10831                 | -0.22757                 | -0.14502                 | -0.07200       | -0.10359         | -0.07526         | -0.15924         | -0.10359         | -0.10260         | -0.10260         |
| $E_{10^6 \text{ rad}}^{\text{atom}} (eV)$        | 0.14803          | 0.14803           | 0.11441      | 0.11441                  | 0.14803                  | 0.14803                  | 0.14803        | 0.14803          | 0.14803          | 0.14803          | 0.14803          | 0.14803          | 0.14803          |
| $E_{10^6 \text{ rad}}^{\text{atom}} (eV)$        | -33.26541        | -33.40711         | -32.82330    | -126.97472               | -67.92207                | -49.80996                | -31.70737      | -33.59732        | -33.49373        | -33.26541        | -33.59732        | -33.18712        | -33.18712        |
| $E_{10^6 \text{ rad}}^{\text{atom}} (eV)$        | -14.63489        | -14.63489         | -14.63489    | -14.63489                | -14.63489                | -14.63489                | -14.63489      | -14.63489        | -14.63489        | -14.63489        | -14.63489        | -14.63489        | -14.63489        |
| $E_{10^6 \text{ rad}}^{\text{atom}} (eV)$        | 0                | 0                 | 0            | -1.16125                 | -13.59844                | -13.59844                | -13.59844      | 0                | 0                | 0                | 0                | 0                | 0                |
| $E_{10^6 \text{ rad}}^{\text{atom}} (eV)$        | 3.99563          | 4.13733           | 3.55352      | 8.61994                  | 12.49186                 | 7.83016                  | 3.32601        | 4.32754          | 4.29921          | 3.97398          | 4.17951          | 3.62128          | 3.91734          |

Table 15.187. The total bond energies of alkyl sulfates calculated using the functional group composition and the energies of Table 15.186 compared to the experimental values [3].

| Formula                                       | Name             | C-O (i)<br>Group | C-O (ii)<br>Group | O-S<br>Group | SO <sub>2</sub><br>Group | CH <sub>3</sub><br>Group | CH <sub>2</sub><br>Group | C-H<br>Group | C-C (a)<br>Group | C-C (b)<br>Group | C-C (c)<br>Group | C-C (d)<br>Group | C-C (e)<br>Group | C-C (f)<br>Group | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond<br>Energy (eV) | Relative Error |
|-----------------------------------------------|------------------|------------------|-------------------|--------------|--------------------------|--------------------------|--------------------------|--------------|------------------|------------------|------------------|------------------|------------------|------------------|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>4</sub> H <sub>9</sub> SO <sub>4</sub> | Dimethyl sulfate | 2                | 0                 | 2            | 1                        | 2                        | 0                        | 0            | 0                | 0                | 0                | 0                | 0                | 0                | 48.734                                  | 48.734                                    | 0.00058        |
| C <sub>4</sub> H <sub>9</sub> SO <sub>4</sub> | Diethyl sulfate  | 0                | 2                 | 2            | 1                        | 2                        | 0                        | 2            | 0                | 0                | 0                | 0                | 0                | 0                | 73.3077                                 | 73.346                                    | 0.00061        |
| C <sub>4</sub> H <sub>9</sub> SO <sub>4</sub> | Dipropyl sulfate | 0                | 2                 | 2            | 1                        | 2                        | 0                        | 4            | 0                | 0                | 0                | 0                | 0                | 0                | 97.6167                                 | 97.609                                    | -0.00008       |





# NITROALKANES ( $C_n H_{2n+2-m} (NO_2)_m$ , $n = 1, 2, 3, 4, 5 \dots \infty$ )

The nitroalkanes,  $C_n H_{2n+2-m} (NO_2)_m$ , comprise a  $NO_2$  functional group and a  $C-N$  functional group. The alkyl portion of the nitroalkane may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and  
 5 methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2 CH$ ) and t-butyl ( $(CH_3)_3 C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  
 10  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in nitroalkanes are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is  $1s^2 2s^2 2p^4$ , and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state  $^3P_2$ . The electron configuration of nitrogen is  $1s^2 2s^2 2p^3$ , and the orbital arrangement given by Eq. (10.134) has  
 15 three unpaired electrons corresponding to the ground state  $^4S_{3/2}$ . The bonding in the nitro ( $NO_2$ ) functional group is similar to that in the  $SO_2$  group given previously. It also has similarities to the bonding in the carbonyl functional group. In the  $NO_2$  group, the two unpaired electrons of the  $O$  atoms form a MO with two unpaired electrons of the nitrogen atom such that the MO comprises a linear combination of two bonds, each of bond order two involving the  
 20 nitrogen AOs and oxygen AOs of both oxygen atoms. The nitrogen atom is then energy matched to the  $C2sp^3$  HO. In nitroalkanes, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)), the  $N$  AO has an energy of  $E(N) = -14.53414 \text{ eV}$ , and the  $O$  AO has an energy of  $E(O) = -13.61806 \text{ eV}$  [38]. To meet the equipotential condition of the union of the  $N=O$   
 25  $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the  $N=O$ -bond MO given by Eqs. (15.68) and (15.70) is

$$\begin{aligned}
 c_2(O \text{ to } N2p \text{ to } C2sp^3 HO) &= \frac{E(O)}{E(N)} c_2(C2sp^3 HO) \\
 &= \frac{-13.61806 \text{ eV}}{-14.53414 \text{ eV}} (0.91771) \\
 &= 0.85987
 \end{aligned}
 \tag{15.140}$$

Since there are two  $O$  atoms in a linear combination that comprises the bonding of the  $NO_2$  group, the unpaired electrons of each  $O$  cancel each others effect such that  $E_{mag}$  is not subtracted from the total energy of  $NO_2$ . Additionally,  $E_T(atom-atom,msp^3.AO) = -3.71673 \text{ eV} = 4(-0.92918 \text{ eV})$  (Eq. (14.513)) is the maximum

5 given the bonding involves four electrons comprising two bonds, each having a bond order of one.

The  $C-N$  group is equivalent to that of primary amines except that the energies corresponding to vibration in the transition state are matched to a nitroalkane and  $\Delta E_{H_2MO}(AO/HO) = -0.72457 \text{ eV}$  for nitroalkane and  $\Delta E_{H_2MO}(AO/HO) = -1.44915 \text{ eV}$  for

10 primary amines. Whereas,  $E_T(atom-atom,msp^3.AO) = -1.44915 \text{ eV}$  for both functional groups. This condition matches the energy of the  $C-N$  group with the  $NO_2$  having  $\Delta E_{H_2MO}(AO/HO) = 0$ .

The symbols of the functional groups of branched-chain nitroalkanes are given in Table 15.189. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and

15 energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of nitroalkanes are given in Tables 15.190, 15.191, and 15.192, respectively. The total energy of each nitroalkane given in Table 15.193 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.192 corresponding to functional-group composition of the molecule.  $E_{mag}$  given by Eq. (15.58) was subtracted for each t-butyl group. The bond angle parameters of nitroalkanes determined using

20 Eqs. (15.79-15.108) are given in Table 15.194.

Table 15.189. The symbols of functional groups of nitroalkanes.

| Functional Group    | Group Symbol |
|---------------------|--------------|
| $NO_2$ group        | $NO_2$       |
| $C-N$               | $C-N$        |
| $CH_3$ group        | $C-H (CH_3)$ |
| $CH_2$ group        | $C-H (CH_2)$ |
| $CH$                | $C-H$        |
| $CC$ bond (n-C)     | $C-C$ (a)    |
| $CC$ bond (iso-C)   | $C-C$ (b)    |
| $CC$ bond (tert-C)  | $C-C$ (c)    |
| $CC$ (iso to iso-C) | $C-C$ (d)    |
| $CC$ (t to t-C)     | $C-C$ (e)    |
| $CC$ (t to iso-C)   | $C-C$ (f)    |

Table 15.190. The geometrical bond parameters of nitroalkanes and experimental values [1].

| Parameter                             | $\text{NO}_2$<br>Group  | $\text{C}-\text{N}$<br>Group | $\text{C}-\text{H}$ ( $\text{CH}_3$ )<br>Group  | $\text{C}-\text{H}$ ( $\text{CH}_2$ )<br>Group  | $\text{C}-\text{C}$ (a)<br>Group | $\text{C}-\text{C}$ (b)<br>Group        | $\text{C}-\text{C}$ (c)<br>Group        | $\text{C}-\text{C}$ (d)<br>Group        | $\text{C}-\text{C}$ (e)<br>Group        | $\text{C}-\text{C}$ (f)<br>Group        |
|---------------------------------------|-------------------------|------------------------------|-------------------------------------------------|-------------------------------------------------|----------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|
| $a$ ( $\text{\AA}$ )                  | 1.33221                 | 1.97794                      | 1.07122                                         | 1.07122                                         | 1.67465                          | 2.12499                                 | 2.10725                                 | 2.12499                                 | 2.10725                                 | 2.10725                                 |
| $c'$ ( $\text{\AA}$ )                 | 1.15421                 | 1.40639                      | 1.04856                                         | 1.05553                                         | 1.05661                          | 1.45744                                 | 1.45164                                 | 1.45744                                 | 1.45164                                 | 1.45164                                 |
| Bond Length<br>$2c'$ ( $\text{\AA}$ ) | 1.22157                 | 1.48846                      | 1.10974                                         | 1.11713                                         | 1.11827                          | 1.54280                                 | 1.53635                                 | 1.54280                                 | 1.53635                                 | 1.53635                                 |
| Exp. Bond Length<br>( $\text{\AA}$ )  | 1.224<br>(nitromethane) | 1.489<br>(nitromethane)      | 1.107<br>(C-H propane)<br>1.117<br>(C-H butane) | 1.107<br>(C-H propane)<br>1.117<br>(C-H butane) | 1.122<br>(isobutane)             | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) | 1.532<br>(propane)<br>1.531<br>(butane) |
| $h_c$ ( $\text{\AA}$ )                | 0.66526                 | 1.39079                      | 1.27295                                         | 1.29569                                         | 1.29924                          | 1.54616                                 | 1.52750                                 | 1.54616                                 | 1.52750                                 | 1.52750                                 |
| $e$                                   | 0.86039                 | 0.71104                      | 0.63380                                         | 0.63159                                         | 0.63095                          | 0.68600                                 | 0.68888                                 | 0.68600                                 | 0.68888                                 | 0.68888                                 |

Table 15.191. The MO to HO intercept geometrical bond parameters of nitroalkanes.  $R, R', R''$  are H or alkyl groups.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{mfp}, \text{AO})$ .

| Bond                               | Atom | $E_T$<br>(eV)<br>Bond 1 | $E_T$<br>(eV)<br>Bond 2 | $E_T$<br>(eV)<br>Bond 3 | $E_T$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>$C_{2sp}^*$<br>(eV) | $r_{\text{final}}$<br>( $\text{\AA}$ ) | $E_{\text{Coulomb}}$<br>(eV)<br>Final | $E(C_{2sp}^*)$<br>(eV)<br>Final | $\theta'$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | $d_1$<br>( $\text{\AA}$ ) | $d_2$<br>( $\text{\AA}$ ) |
|------------------------------------|------|-------------------------|-------------------------|-------------------------|-------------------------|----------------------------------------------|----------------------------------------|---------------------------------------|---------------------------------|---------------------------|----------------------------|----------------------------|---------------------------|---------------------------|
| $RN(O)=O$                          | O    | -0.92918                | 0                       | 0                       | 0                       | -15.75493                                    | 0.86359                                | -15.75493                             |                                 | 135.25                    | 44.75                      | 66.05                      | 0.54089                   | 0.61333                   |
| $RN(O)=O$                          | N    | -0.92918                | -0.92918                | -0.72457                | 0                       | -17.40869                                    | 0.78155                                | -17.40869                             |                                 | 131.57                    | 48.43                      | 61.50                      | 0.63538                   | 0.51864                   |
| $H_3C-NO_2$                        | C    | -0.72457                | 0                       | 0                       | 0                       | -152.34026                                   | 0.91771                                | -15.53033                             | -15.53946                       | 80.47                     | 99.53                      | 38.35                      | 1.55123                   | 0.14484                   |
| $RH_2C-NO_2$                       | N    | -0.92918                | -0.92918                | -0.72457                | 0                       | -17.40869                                    | 0.78155                                | -17.40869                             |                                 | 69.30                     | 110.70                     | 31.71                      | 1.68259                   | 0.27620                   |
| $R=H, \text{alkyl}$                | C    | -0.72457                | -0.92918                | 0                       | 0                       | -153.26945                                   | 0.91771                                | -16.47951                             | -16.28864                       | 74.96                     | 105.04                     | 34.98                      | 1.62061                   | 0.21422                   |
| $-H_2C-NO_2$                       | C    | -0.92918                | 0                       | 0                       | 0                       | -152.34487                                   | 0.86359                                | -15.75493                             | -15.5407                        | 77.49                     | 102.51                     | 41.48                      | 1.23564                   | 0.18708                   |
| $C-H$ ( $\text{CH}_3$ )            | C    | -0.92918                | 0                       | 0                       | 0                       | -153.47406                                   | 0.91771                                | -16.68412                             | -16.49525                       | 68.47                     | 111.53                     | 35.84                      | 1.35486                   | 0.22933                   |
| $C-H$ ( $\text{CH}_2$ )            | C    | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40524                                   | 0.77247                                | -17.61530                             | -17.42244                       | 61.10                     | 118.90                     | 31.37                      | 1.42988                   | 0.37526                   |
| $H_3C-C, H_3C-H_2-$<br>(C-C (a))   | C    | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                   | 0.86359                                | -15.75493                             | -15.56407                       | 63.82                     | 116.18                     | 30.08                      | 1.83879                   | 0.38106                   |
| $R-H_2C-C, H_2C-H_2-$<br>(C-C (b)) | C    | -0.92918                | -0.92918                | -0.92918                | 0                       | -153.47406                                   | 0.81549                                | -16.68412                             | -16.49325                       | 56.41                     | 125.59                     | 26.06                      | 1.90590                   | 0.45117                   |
| $R-H_2C-C, H_2C-H_2-$<br>(C-C (c)) | C    | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40524                                   | 0.77247                                | -17.61530                             | -17.42244                       | 48.30                     | 131.70                     | 21.90                      | 1.97162                   | 0.51388                   |
| $R-H_2C-C, H_2C-H_2-$<br>(C-C (d)) | C    | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -154.71860                                   | 0.75889                                | -17.92866                             | -17.73779                       | 48.21                     | 131.79                     | 21.74                      | 1.95734                   | 0.50570                   |
| $R-H_2C-C, H_2C-H_2-$<br>(C-C (e)) | C    | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40524                                   | 0.77247                                | -17.61530                             | -17.42244                       | 48.30                     | 131.70                     | 21.90                      | 1.97162                   | 0.51388                   |
| $R-H_2C-C, H_2C-H_2-$<br>(C-C (f)) | C    | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.51939                                   | 0.76165                                | -17.92866                             | -17.73779                       | 50.04                     | 129.96                     | 22.66                      | 1.94462                   | 0.49298                   |
| $R-H_2C-C, H_2C-H_2-$<br>(C-C (g)) | C    | -0.72457                | -0.92918                | -0.92918                | 0                       | -154.19665                                   | 0.78155                                | -17.40869                             | -17.21783                       | 52.78                     | 127.22                     | 24.04                      | 1.92443                   | 0.47279                   |
| $R-H_2C-C, H_2C-H_2-$<br>(C-C (h)) | C    | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.51939                                   | 0.76165                                | -17.92866                             | -17.73779                       | 50.04                     | 129.96                     | 22.66                      | 1.94462                   | 0.49298                   |

Table 15.192. The energy parameters (eV) of functional groups of nitroalkanes.

| Parameters                    | $NO_2$ Group | $C-N$ Group | $CH_3$ Group | $CH_2$ Group | $C-H$ Group | $C-C$ (a) Group | $C-C$ (b) Group | $C-C$ (c) Group | $C-C$ (d) Group | $C-C$ (e) Group | $C-C$ (f) Group |
|-------------------------------|--------------|-------------|--------------|--------------|-------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $n_1$                         | 2            | 1           | 3            | 2            | 1           | 1               | 1               | 1               | 1               | 1               | 1               |
| $n_2$                         | 0            | 0           | 2            | 1            | 0           | 0               | 0               | 0               | 0               | 0               | 0               |
| $n_3$                         | 0            | 0           | 0            | 0            | 0           | 0               | 0               | 0               | 0               | 0               | 0               |
| $C_1$                         | 0.5          | 0.5         | 0.75         | 0.75         | 0.75        | 0.5             | 0.5             | 0.5             | 0.5             | 0.5             | 0.5             |
| $C_2$                         | 1            | 1           | 1            | 1            | 1           | 1               | 1               | 1               | 1               | 1               | 1               |
| $C_3$                         | 1            | 1           | 1            | 1            | 1           | 1               | 1               | 1               | 1               | 1               | 1               |
| $C_4$                         | 0.85987      | 0.91140     | 0.91771      | 0.91771      | 0.91771     | 0.91771         | 0.91771         | 0.91771         | 0.91771         | 0.91771         | 0.91771         |
| $C_5$                         | 0            | 0           | 0            | 1            | 1           | 0               | 0               | 0               | 1               | 1               | 0               |
| $C_6$                         | 4            | 2           | 1            | 1            | 1           | 2               | 2               | 2               | 2               | 2               | 2               |
| $C_7$                         | 0            | 0           | 3            | 2            | 1           | 0               | 0               | 0               | 0               | 0               | 0               |
| $C_8$                         | 0.5          | 0.5         | 0.75         | 0.75         | 0.75        | 0.5             | 0.5             | 0.5             | 0.5             | 0.5             | 0.5             |
| $C_{9a}$                      | 1            | 1           | 1            | 1            | 1           | 1               | 1               | 1               | 1               | 1               | 1               |
| $V_1$ (eV)                    | -106.90919   | -31.36351   | -107.32728   | -70.41425    | -35.12015   | -28.79214       | -28.79214       | -29.10112       | -28.79214       | -29.10112       | -29.10112       |
| $V_2$ (eV)                    | 25.57588     | 9.67426     | 38.97278     | 25.78002     | 12.87680    | 9.33352         | 9.33352         | 9.37273         | 9.33352         | 9.37273         | 9.37273         |
| $T_1$ (eV)                    | 40.12475     | 7.92833     | 32.53914     | 21.06675     | 10.48582    | 6.77464         | 6.77464         | 6.90500         | 6.77464         | 6.90500         | 6.90500         |
| $V_m$ (eV)                    | -20.06238    | -3.96416    | -16.26957    | -10.53337    | -5.24291    | -3.38732        | -3.38732        | -3.45250        | -3.38732        | -3.45250        | -3.45250        |
| $E_{1,100}$ (eV)              | 0            | -14.63489   | -15.56407    | -15.56407    | -14.63489   | -15.56407       | -15.56407       | -15.56407       | -15.56407       | -15.56407       | -15.56407       |
| $\Delta E_{1,100}$ (eV)       | 0            | -0.72457    | 0            | 0            | 0           | 0               | 0               | 0               | 0               | 0               | 0               |
| $E_{1,100}$ (eV)              | 0            | -13.91032   | -15.56407    | -15.56407    | -14.63489   | -15.56407       | -15.56407       | -15.56407       | -15.56407       | -15.56407       | -15.56407       |
| $E_{1,100}$ (eV)              | -63.27093    | -31.63540   | -67.69451    | -49.66493    | -31.63533   | -31.63537       | -31.63537       | -31.63537       | -31.63537       | -31.63537       | -31.63537       |
| $E_{1,100}$ (eV)              | -3.71673     | -1.44915    | 0            | 0            | 0           | -1.85836        | -1.85836        | -1.44915        | -1.85836        | -1.44915        | -1.44915        |
| $E_{1,100}$ (eV)              | -66.98746    | -33.08452   | -67.69450    | -49.66493    | -31.63537   | -33.49373       | -33.49373       | -33.49373       | -33.49373       | -33.49373       | -33.49373       |
| $\omega$ [ $10^{15}$ rad / s] | 19.0113      | 10.5087     | 24.9286      | 24.2751      | 24.1759     | 9.43699         | 9.43699         | 15.4846         | 9.43699         | 9.43699         | 9.43699         |
| $E_{1,100}$ (eV)              | 12.51354     | 6.91703     | 16.40846     | 15.97831     | 15.91299    | 6.21159         | 6.21159         | 10.19220        | 6.21159         | 6.21159         | 6.21159         |
| $E_{1,100}$ (eV)              | -0.23440     | -0.17214    | -0.25352     | -0.25017     | -0.24966    | -0.16515        | -0.16515        | -0.20896        | -0.16515        | -0.16515        | -0.16515        |
| $E_{1,100}$ (eV)              | 0.19542      | 0.10539     | 0.35532      | 0.35532      | 0.35532     | 0.12312         | 0.12312         | 0.09944         | 0.12312         | 0.12312         | 0.12312         |
| $E_{1,100}$ (eV)              | -0.13769     | -0.11945    | -0.22757     | -0.14502     | -0.07200    | -0.10359        | -0.07266        | -0.15924        | -0.10359        | -0.10359        | -0.10359        |
| $E_{1,100}$ (eV)              | 0.11441      | 0.14803     | 0.14803      | 0.14803      | 0.14803     | 0.14803         | 0.14803         | 0.14803         | 0.14803         | 0.14803         | 0.14803         |
| $E_{1,100}$ (eV)              | -67.26284    | -33.20397   | -67.92207    | -49.80996    | -31.70737   | -33.59732       | -33.59732       | -33.24376       | -33.59732       | -33.59732       | -33.59732       |
| $E_{1,100}$ (eV)              | -14.63489    | -14.63489   | -14.63489    | -14.63489    | -14.63489   | -14.63489       | -14.63489       | -14.63489       | -14.63489       | -14.63489       | -14.63489       |
| $E_{1,100}$ (eV)              | 0            | 0           | -13.59844    | -13.59844    | -13.59844   | 0               | 0               | 0               | 0               | 0               | 0               |
| $E_{1,100}$ (eV)              | 8.72329      | 3.93419     | 12.49186     | 7.83016      | 3.32601     | 4.32754         | 4.29921         | 3.97398         | 4.17951         | 3.62128         | 3.91734         |

Table 15.193. The total bond energies of nitroalkanes calculated using the functional group composition and the energies of Table 15.192 compared to the experimental values [2]. The magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_{1,100}$  (eV) values based on composition is given by (15.38).

| Formula         | Name           | $NO_2$ Group | $C-N$ Group | $CH_3$ Group | $CH_2$ Group | $CH$ Group | $C-C$ (a) | $C-C$ (b) | $C-C$ (c) | $C-C$ (d) | $C-C$ (e) | $C-C$ (f) | $E_{mag}$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|-----------------|----------------|--------------|-------------|--------------|--------------|------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------------------------------|-------------------------------------|----------------|
| $CH_3NO_2$      | Nitromethane   | 1            | 1           | 1            | 0            | 0          | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 25.14934                          | 25.107                              | -0.00168       |
| $C_2H_5NO_2$    | Nitroethane    | 1            | 1           | 1            | 1            | 0          | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 37.30704                          | 37.292                              | -0.00040       |
| $C_3H_7NO_2$    | 1-Nitropropane | 1            | 1           | 2            | 2            | 0          | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 49.46474                          | 49.451                              | -0.00028       |
| $C_4H_9NO_2$    | 2-Nitropropane | 1            | 2           | 0            | 1            | 0          | 2         | 0         | 0         | 0         | 0         | 0         | 0         | 49.56563                          | 49.602                              | 0.00074        |
| $C_4H_9NO_2$    | 1-Nitrobutane  | 1            | 2           | 0            | 0            | 0          | 3         | 0         | 0         | 0         | 0         | 0         | 0         | 61.62244                          | 61.601                              | -0.00036       |
| $C_5H_{11}NO_2$ | 2-Nitropentane | 1            | 3           | 0            | 0            | 0          | 0         | 3         | 0         | 0         | 0         | 0         | -1        | 61.90697                          | 61.945                              | 0.00061        |
| $C_6H_{13}NO_2$ | 1-Nitrohexane  | 1            | 4           | 0            | 0            | 0          | 4         | 0         | 0         | 0         | 0         | 0         | 0         | 73.28014                          | 73.259                              | -0.00028       |

Table 15.194. The bond angle parameters of nitroalkanes and experimental values [1]. In the calculation of  $\theta_2$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{usp}^3, \text{AO})$ .

| Atoms of Angle                                          | $2c_1$<br>Bond 1<br>( $\theta_1$ ) | $2c_2$<br>Bond 2<br>( $\theta_2$ ) | $2c_3$<br>Terminal<br>Atom ( $\theta_3$ ) | $E_{\text{calc}}^{\text{calc}}$<br>or<br>$E^{\text{exp}}$<br>Atom 1 | Atom 1<br>Hybridization<br>Designation<br>(Table 15.3.A) | $c_1$<br>Atom 1 | $c_2$<br>Atom 2        | $c_3$<br>Atom 3 | $c_4$ | $c_5$ | $E_T$<br>(eV) | $\theta_r$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | Cal. $\theta$<br>( $^\circ$ ) | Exp. $\theta$<br>( $^\circ$ )                                 |
|---------------------------------------------------------|------------------------------------|------------------------------------|-------------------------------------------|---------------------------------------------------------------------|----------------------------------------------------------|-----------------|------------------------|-----------------|-------|-------|---------------|----------------------------|----------------------------|----------------------------|-------------------------------|---------------------------------------------------------------|
| $\angle \text{N-C}_\alpha\text{-H}$                     | 2.81279                            | 2.09711                            | 3.0665                                    | -14.82575                                                           | 1                                                        | 0.91771         | 0.9140<br>(Eq. 15.116) | 0.75            | 1     | 0.75  | 0             |                            |                            |                            | 106.87                        | 107<br>(nitromethane)                                         |
| $\angle \text{O}_\alpha\text{-N-O}_\beta$               | 2.30843                            | 2.30843                            | 4.1231                                    | -16.68411                                                           | 24                                                       | 0.81549         | 0.81549                | 1               | 1     | 1     | -1.44915      |                            |                            |                            | 126.52                        | 125.3<br>(nitromethane)                                       |
| $\angle \text{H-C}_\alpha\text{-H}$                     | 2.11106                            | 2.11106                            | 3.4252                                    | -15.75493                                                           | 7                                                        | 0.86359         | 1                      | 1               | 1     | 0.75  | 0             |                            |                            |                            | 108.44                        | 107<br>(propane)                                              |
| $\angle \text{C}_\alpha\text{-C}_\beta\text{-C}_\gamma$ |                                    |                                    |                                           |                                                                     |                                                          |                 |                        |                 |       |       |               | 69.51                      |                            |                            |                               | 112<br>(propane)<br>115.8<br>(butane)<br>110.8<br>(isobutane) |
| $\angle \text{C}_\alpha\text{-C}_\beta\text{-H}$        |                                    |                                    |                                           |                                                                     |                                                          |                 |                        |                 |       |       |               | 69.51                      |                            |                            |                               | 110.49<br>(butane)<br>111.4<br>(isobutane)                    |
| $\angle \text{H-C}_\alpha\text{-H}$                     | 2.09711                            | 2.09711                            | 3.4252                                    | -15.75493                                                           | 7                                                        | 0.86359         | 1                      | 1               | 1     | 0.75  | 0             |                            |                            |                            | 109.50                        |                                                               |
| $\angle \text{C}_\alpha\text{-C}_\beta\text{-C}_\gamma$ |                                    |                                    |                                           |                                                                     |                                                          |                 |                        |                 |       |       |               | 70.56                      |                            |                            | 109.44                        |                                                               |
| $\angle \text{C}_\alpha\text{-C}_\beta\text{-H}$        |                                    |                                    |                                           |                                                                     |                                                          |                 |                        |                 |       |       |               | 70.56                      |                            |                            | 109.44                        |                                                               |
| $\angle \text{C}_\alpha\text{-C}_\beta\text{-C}_\gamma$ | 2.91547                            | 2.91547                            | 4.7958                                    | -16.68412                                                           | 25                                                       | 0.81549         | 0.81549                | 1               | 1     | 1     | -1.53836      |                            |                            |                            | 110.67                        | 110.8<br>(isobutane)                                          |
| $\angle \text{C}_\alpha\text{-C}_\beta\text{-H}$        | 2.91547                            | 2.11323                            | 4.1633                                    | -15.55033                                                           | 5                                                        | 0.87495         | 0.91771                | 0.75            | 1     | 0.75  | 0             |                            |                            |                            | 110.76                        |                                                               |
| $\angle \text{C}_\alpha\text{-C}_\beta\text{-H}$        | 2.91547                            | 2.09711                            | 4.1633                                    | -15.55033                                                           | 5                                                        | 0.87495         | 0.91771                | 0.75            | 1     | 0.75  | 0             |                            |                            |                            | 111.27                        | 111.4<br>(isobutane)                                          |
| $\angle \text{C}_\alpha\text{-C}_\beta\text{-C}_\gamma$ | 2.90327                            | 2.90327                            | 4.7958                                    | -15.55033                                                           | 5                                                        | 0.87495         | 0.91771                | 0.75            | 1     | 0.75  | -1.53836      |                            |                            |                            | 111.27                        | 111.4<br>(isobutane)                                          |
| $\angle \text{C}_\alpha\text{-C}_\beta\text{-C}_\gamma$ |                                    |                                    |                                           |                                                                     |                                                          |                 |                        |                 |       |       |               | 72.50                      |                            |                            | 107.50                        |                                                               |

# ALKYL NITRITES ( $C_nH_{2n+2-m}(NO_2)_m$ , $n = 1, 2, 3, 4, 5 \dots \infty$ )

The alkyl nitrites,  $C_nH_{2n+2-m}(NO_2)_m$ , comprise a  $RC-O-NO$  moiety that comprises  $C-O$ ,  $O-N$ , and  $NO$  functional groups. The alkyl portion of the alkyl nitrite may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise 5 methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, 10 and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in alkyl nitrites are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is  $1s^2 2s^2 2p^4$ , and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state  $^3P_2$ . The electron configuration of nitrogen is  $1s^2 2s^2 2p^3$ , and the orbital arrangement given by Eq. (10.134) has 15 three unpaired electrons corresponding to the ground state  $^4S_{3/2}$ . The bonding in the nitro ( $NO$ ) functional group is similar to that in the  $SO$  group given previously. It also has similarities to the bonding in the carbonyl functional group. In the  $NO$  group, the two unpaired electrons of the  $O$  atom form a MO with two unpaired electrons of the nitrogen atom such that the MO comprises a double bond. The nitrogen atom is then energy matched to the  $O-N$  functional 20 group that is further energy matched to the  $C2sp^3$  HO of the  $C-O$  functional group. To meet the equipotential condition of the union of the  $N=O$   $H_2$ -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor  $c_2$  of Eq. (15.51) for the  $N=O$ -bond MO given by Eq. (15.140) is  $c_2(O \text{ to } N2p \text{ to } C2sp^3HO) = 0.85987$ .

As in the case of the carbonyl group, two unpaired  $O$  electrons result upon bond 25 breakage of the  $N=O$  bond which requires that two times  $E_{mag}$  of oxygen (Eq. (15.59)) be subtracted from the total energy of  $NO$ . Additionally,  $E_r(atom - atom, msp^3.AO)$  and  $\Delta E_{H_2MO}(AO/HO)$  are equal to  $-0.92918 \text{ eV}$  (Eq. (14.513)) which matches the energy of the  $N=O$  bond with the contiguous  $O-N$  bond and matches the energy contribution of an oxygen atom.

The  $O-N$  functional group comprise a single-bond,  $H_2$ -type-ellipsoidal-MO between the remaining unpaired nitrogen electron and an unpaired electron of the second oxygen atom which further forms a single bond with the  $C2sp^3$  HO of the  $C-O$  functional group. In alkyl nitrites, the hybridization factor  $c_2$  of Eq. (15.52) for the  $C-O$ -bond MO given by Eq. 5 (15.114) is  $c_2(C2sp^3HO \text{ to } O) = 0.85395$ . The hybridization factor  $c_2$  of Eq. (15.52) for a  $C-N$ -bond MO given by Eq. (15.116) is  $c_2(C2sp^3HO \text{ to } N) = 0.91140$ . Thus, the hybridization factor  $c_2$  of Eq. (15.52) for  $O-N$  that bridges the  $C-O$  and  $N=O$  bonds given by Eq. (15.69) is

$$c_2(N2p \text{ to } O2p) = \frac{c_2(C2sp^3HO \text{ to } N)}{c_2(C2sp^3HO \text{ to } O)} = \frac{0.91140}{0.85395} = 1.06727 \quad (15.141)$$

10  $E_r(atom - atom, msp^3 AO) = -0.92918 \text{ eV}$  in order to match the energy of the  $NO$  group and  $E(AO / HO) = -15.35946 \text{ eV}$  in order to match the  $C-O$  functional group.

The  $C-O$  functional group is equivalent to that of an ether as given in the corresponding section except that  $E_r(atom - atom, msp^3 AO)$  and  $\Delta E_{H_2MO}(AO / HO)$  are both  $-0.72457 \text{ eV}$  which matches the energy contribution of an independent  $C2sp^3$  HO (Eq. 15 (14.151)). Also, the energy terms corresponding to the oscillation of the bond in the transition state are matched to a nitrite.

The symbols of the functional groups of branched-chain alkyl nitrites are given in Table 15.195. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl nitrites are given in Tables 20 15.196, 15.197, and 15.198, respectively. The total energy of each alkyl nitrite given in Table 15.199 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.198 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl nitrites determined using Eqs. (15.79-15.108) are given in Table 15.200.



Table 15.195. The symbols of functional groups of alkyl nitriles.

| Functional Group      | Group Symbol           |
|-----------------------|------------------------|
| NO group              | NO                     |
| O-N                   | O-N                    |
| C-O                   | C-O                    |
| CH <sub>3</sub> group | C-H (CH <sub>3</sub> ) |
| CH <sub>2</sub> group | C-H (CH <sub>2</sub> ) |
| CH                    | C-H                    |
| CC bond (n-C)         | C-C' (a)               |
| CC bond (iso-C)       | C-C' (b)               |
| CC bond (tert-C)      | C-C' (c)               |
| CC (iso to iso-C)     | C-C' (d)               |
| CC (t to t-C)         | C-C' (e)               |
| CC (t to iso-C)       | C-C' (f)               |

Table 15.196. The geometrical bond parameters of alkyl nitriles and experimental values [1].

| Parameter                | NO Group                                          | O-N Group                                           | C-O Group              | C-H (CH <sub>3</sub> ) Group              | C-H (CH <sub>2</sub> ) Group              | C-H Group         | C-C (a) Group                     | C-C (b) Group                     | C-C (c) Group                     | C-C (d) Group                     | C-C (e) Group                     | C-C (f) Group                     |
|--------------------------|---------------------------------------------------|-----------------------------------------------------|------------------------|-------------------------------------------|-------------------------------------------|-------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| $a$ (Å)                  | 1.32255                                           | 1.76440                                             | 1.85327                | 1.64920                                   | 1.67122                                   | 1.67465           | 2.12499                           | 2.12499                           | 2.10725                           | 2.12499                           | 2.10725                           | 2.10725                           |
| $c'$ (Å)                 | 1.15002                                           | 1.32831                                             | 1.36135                | 1.04856                                   | 1.05553                                   | 1.05661           | 1.45744                           | 1.45744                           | 1.45164                           | 1.45744                           | 1.45164                           | 1.45164                           |
| Bond Length<br>$2c'$ (Å) | 1.21713                                           | 1.40582                                             | 1.44079                | 1.10974                                   | 1.11713                                   | 1.11827           | 1.54280                           | 1.54280                           | 1.55635                           | 1.54280                           | 1.55635                           | 1.55635                           |
| Exp. Bond Length<br>(Å)  | 1.205 (methyl nitrate)<br>1.2 (HNO <sub>2</sub> ) | 1.402 (methyl nitrate)<br>1.432 (HNO <sub>2</sub> ) | 1.437 (methyl nitrate) | 1.107 (C-H propane)<br>1.117 (C-H butane) | 1.107 (C-H propane)<br>1.117 (C-H butane) | 1.122 (isobutane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) |
| $h, c$ (Å)               | 0.65314                                           | 1.16134                                             | 1.25751                | 1.27295                                   | 1.29569                                   | 1.29924           | 1.54616                           | 1.54616                           | 1.52750                           | 1.54616                           | 1.52750                           | 1.52750                           |
| $\sigma$                 | 0.86955                                           | 0.75284                                             | 0.73457                | 0.63580                                   | 0.63159                                   | 0.65095           | 0.68600                           | 0.68600                           | 0.68888                           | 0.68600                           | 0.68888                           | 0.68888                           |

Table 15 197. The MO to HO intercept geometrical bond parameters of alkyl nitriles.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{map}^2, \text{AO})$ .

| Bond                                      | Atom           | $E_T$<br>(eV)<br>Bond 1 | $E_T$<br>(eV)<br>Bond 2 | $E_T$<br>(eV)<br>Bond 3 | $E_T$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>(eV) | $r_{\text{final}}$<br>(a <sub>0</sub> ) | $r_{\text{final}}$<br>(a <sub>0</sub> ) | $E_{\text{calculated}}$<br>(eV)<br>Final | $E(\text{C}2\text{sp}^2)$<br>(eV)<br>Final | $\theta'$<br>(°) | $\theta_1$<br>(°) | $\theta_2$<br>(°) | $d_1$<br>(a <sub>0</sub> ) | $d_2$<br>(a <sub>0</sub> ) |
|-------------------------------------------|----------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------------|-----------------------------------------|-----------------------------------------|------------------------------------------|--------------------------------------------|------------------|-------------------|-------------------|----------------------------|----------------------------|
| $RON=O$                                   | O              | -0.46459                | 0                       | 0                       | 0                       | -15.20834                     | 1.00000                                 | 0.88993                                 | -15.20834                                |                                            | 137.15           | 42.85             | 67.90             | 0.9764                     | 0.63238                    |
| $RON=O$                                   | N              | -0.46459                | -0.46459                | 0                       | 0                       | -15.75493                     | 0.93084                                 | 0.86359                                 | -15.75493                                |                                            | 136.09           | 43.91             | 66.48             | 0.92781                    | 0.62221                    |
| $RO_2=NO_2$                               | O <sub>1</sub> | -0.46459                | -0.36229                | 0                       | 0                       | -15.63263                     | 1.00000                                 | 0.86923                                 | -15.63263                                |                                            | 99.22            | 80.78             | 47.63             | 1.18905                    | 0.19325                    |
| $RO_2=NO_2$                               | N              | -0.46459                | -0.46459                | 0                       | 0                       | -15.75493                     | 0.93084                                 | 0.86359                                 | -15.75493                                |                                            | 98.78            | 81.22             | 47.30             | 1.19655                    | 0.13175                    |
| $RH_2C=O_2NO_2$                           | O <sub>1</sub> | -0.36229                | -0.46459                | 0                       | 0                       | -15.63263                     | 1.00000                                 | 0.86923                                 | -15.63263                                |                                            | 91.43            | 88.57             | 43.71             | 1.33962                    | 0.02173                    |
| $H_2C=O_2NO_2$                            | C              | -0.36229                | 0                       | 0                       | 0                       | -15.19708                     | 0.91771                                 | 0.89582                                 | -15.18804                                | -14.99717                                  | 93.71            | 86.29             | 45.31             | 1.30342                    | 0.05793                    |
| $-CH_2H_2C=O_2NO_2$                       | C              | -0.36229                | -0.92918                | 0                       | 0                       | -152.90716                    | 0.91771                                 | 0.84418                                 | -16.11722                                | -15.92636                                  | 89.16            | 90.84             | 42.16             | 1.37373                    | 0.01238                    |
| $C-H(C_1)$                                | C              | -0.92918                | 0                       | 0                       | 0                       | -152.54487                    | 0.91771                                 | 0.86359                                 | -15.75493                                | -15.56407                                  | 77.49            | 102.51            | 41.48             | 1.23564                    | 0.18708                    |
| $C-H(C_2)$                                | C              | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                    | 0.91771                                 | 0.81549                                 | -16.08412                                | -16.49325                                  | 68.47            | 111.53            | 35.84             | 1.35486                    | 0.29933                    |
| $C-H(C_3)$                                | C              | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                    | 0.91771                                 | 0.77247                                 | -17.61330                                | -17.42244                                  | 61.10            | 118.90            | 31.37             | 1.42988                    | 0.37326                    |
| $H_2C_2H_2CH_2CH_2-$<br>(C-C (a))         | C              | -0.92918                | 0                       | 0                       | 0                       | -152.54487                    | 0.91771                                 | 0.86359                                 | -15.75493                                | -15.56407                                  | 63.82            | 116.18            | 30.08             | 1.33879                    | 0.38106                    |
| $H_2C_2H_2CH_2CH_2-$<br>(C-C (b))         | C              | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                    | 0.91771                                 | 0.81549                                 | -16.08412                                | -16.49325                                  | 56.41            | 123.59            | 26.06             | 1.90890                    | 0.43117                    |
| $R-H_2C(R'-H_2C)(R'')HCH_2-$<br>(C-C (c)) | C              | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                    | 0.91771                                 | 0.77247                                 | -17.61330                                | -17.42244                                  | 48.30            | 131.70            | 21.90             | 1.97162                    | 0.51388                    |
| $R-H_2C(R'-H_2C)(R'')HCH_2-$<br>(C-C (d)) | C              | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -154.17660                    | 0.91771                                 | 0.73869                                 | -17.92866                                | -17.73779                                  | 48.21            | 131.79            | 21.74             | 1.95734                    | 0.50570                    |
| $rac(H_2C_2H_2CH_2CH_2-)$<br>(C-C (e))    | C              | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                    | 0.91771                                 | 0.77247                                 | -17.61330                                | -17.42244                                  | 48.30            | 131.70            | 21.90             | 1.97162                    | 0.51388                    |
| $rac(H_2C_2H_2CH_2CH_2-)$<br>(C-C (f))    | C              | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.51399                    | 0.91771                                 | 0.67665                                 | -17.92866                                | -17.73779                                  | 50.04            | 129.96            | 22.66             | 1.94462                    | 0.49298                    |
| $rac(H_2C_2H_2CH_2CH_2-)$<br>(C-C (g))    | C              | -0.72457                | -0.92918                | -0.92918                | 0                       | -154.19663                    | 0.91771                                 | 0.78155                                 | -17.40869                                | -17.21783                                  | 52.78            | 127.22            | 24.04             | 1.92443                    | 0.47279                    |
| $rac(H_2C_2H_2CH_2CH_2-)$<br>(C-C (h))    | C              | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.51399                    | 0.91771                                 | 0.67665                                 | -17.92866                                | -17.73779                                  | 50.04            | 129.96            | 22.66             | 1.94462                    | 0.49298                    |

Table 15.198. The energy parameters (eV) of functional groups of alkyl nitriles.

| Parameters                             | NO Group   | O-N Group | C-O Group | CH <sub>3</sub> Group | CH <sub>2</sub> Group | C-H Group      | C-C (a) Group | C-C (b) Group | C-C (c) Group | C-C (d) Group | C-C (e) Group | C-C (f) Group |
|----------------------------------------|------------|-----------|-----------|-----------------------|-----------------------|----------------|---------------|---------------|---------------|---------------|---------------|---------------|
| $\eta_1$                               | 2          | 1         | 1         | 3                     | 2                     | 1              | 1             | 1             | 1             | 1             | 1             | 1             |
| $\eta_2$                               | 0          | 0         | 0         | 2                     | 1                     | 0              | 0             | 0             | 0             | 0             | 0             | 0             |
| $\eta_3$                               | 0          | 0         | 0         | 0                     | 0                     | 0              | 0             | 0             | 0             | 0             | 0             | 0             |
| $C_1'$                                 | 0.5        | 0.5       | 0.5       | 0.75                  | 0.75                  | 0.75           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           |
| $C_2'$                                 | 1          | 1         | 1         | 1                     | 1                     | 1              | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_3'$                                 | 1          | 1         | 1         | 1                     | 1                     | 1              | 1             | 1             | 1             | 1             | 1             | 1             |
| $C_4'$                                 | 0.85987    | 1.06727   | 0.85395   | 0.91771               | 0.91771               | 0.91771        | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       | 0.91771       |
| $C_5'$                                 | 2          | 0         | 0         | 0                     | 1                     | 1              | 0             | 0             | 0             | 1             | 1             | 0             |
| $C_6'$                                 | 4          | 2         | 2         | 1                     | 1                     | 1              | 2             | 2             | 2             | 2             | 2             | 2             |
| $C_7'$                                 | 0          | 0         | 0         | 3                     | 2                     | 1              | 0             | 0             | 0             | 0             | 0             | 0             |
| $C_{in}$                               | 0.5        | 0.5       | 0.5       | 0.75                  | 0.75                  | 0.75           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           | 0.5           |
| $C_{out}$                              | 1          | 1         | 1         | 1                     | 1                     | 1              | 1             | 1             | 1             | 1             | 1             | 1             |
| $V_c$ (eV)                             | -108.34117 | -42.83043 | -32.04173 | -107.32728            | -70.41425             | -35.12015      | -28.79214     | -28.79214     | -28.79214     | -28.79214     | -28.79214     | -28.79214     |
| $V_r$ (eV)                             | 23.66182   | 20.48593  | 9.94536   | 38.92728              | 25.78002              | 12.87680       | 9.33352       | 9.33352       | 9.33352       | 9.33352       | 9.33352       | 9.33352       |
| $T_r$ (eV)                             | 40.95920   | 12.13739  | 8.64465   | 32.53914              | 21.06675              | 10.48582       | 6.77464       | 6.77464       | 6.77464       | 6.77464       | 6.77464       | 6.77464       |
| $V_m$ (eV)                             | -20.47960  | -6.06870  | -4.32232  | -16.26957             | -10.53337             | -5.24291       | -3.38732      | -3.38732      | -3.38732      | -3.38732      | -3.38732      | -3.38732      |
| $E_{(w,m)}$ (eV)                       | 0          | -15.35946 | -14.63489 | -15.36407             | -15.36407             | -14.63489      | -15.36407     | -15.36407     | -15.36407     | -15.36407     | -15.36407     | -15.36407     |
| $\Delta E_{(1,1,1)}$ (eV)              | -0.92918   | 0         | -0.72457  | 0                     | 0                     | 0              | 0             | 0             | 0             | 0             | 0             | 0             |
| $E_{(w,m)}$ (eV)                       | 0.92918    | -15.35946 | -13.91032 | -15.36407             | -15.36407             | -14.63489      | -15.36407     | -15.36407     | -15.36407     | -15.36407     | -15.36407     | -15.36407     |
| $E_{(1,2,m)}$ (eV)                     | -63.27057  | -31.63527 | -31.63537 | -67.69451             | -49.66495             | -31.63533      | -31.63537     | -31.63537     | -31.63537     | -31.63537     | -31.63537     | -31.63537     |
| $F_r$ (atom-atom, $mnp^*, d(t)$ ) (eV) | -0.92918   | -0.92918  | -0.72457  | 0                     | 0                     | 0              | -1.85836      | -1.85836      | -1.85836      | -1.85836      | -1.85836      | -1.85836      |
| $F_r$ (eV)                             | -64.19992  | -32.56455 | -32.35994 | -67.69450             | -49.66493             | -31.63537      | -33.49573     | -33.49573     | -33.49573     | -33.49573     | -33.49573     | -33.49573     |
| $\omega$ ( $10^5$ rad/s)               | 19.2199    | 23.3578   | 20.7301   | 24.9286               | 24.2751               | 24.1759        | 9.43699       | 9.43699       | 9.43699       | 9.43699       | 9.43699       | 9.43699       |
| $F_r$ (eV)                             | 12.65089   | 15.37450  | 13.64490  | 16.40846              | 15.97831              | 15.91299       | 6.21159       | 6.21159       | 6.21159       | 6.21159       | 6.21159       | 6.21159       |
| $\bar{E}_r$ (eV)                       | -0.22587   | 0.25261   | -0.23648  | -0.23532              | -0.25017              | -0.24966       | -0.16515      | -0.16515      | -0.16515      | -0.16515      | -0.16515      | -0.16515      |
| $\bar{F}_{rm}$ (eV)                    | 0.20396    | 0.10725   | 0.13663   | 0.35532               | 0.35532               | 0.35532        | 0.12312       | 0.12312       | 0.12312       | 0.12312       | 0.12312       | 0.12312       |
| $\bar{E}_{rm}$ (eV)                    | [46]       | [47]      | [21]      | (Eq. (13.458))        | (Eq. (13.458))        | (Eq. (13.458)) | [4]           | [5]           | [2]           | [2]           | [2]           | [2]           |
| $\bar{E}_{rm}$ (eV)                    | -0.12390   | 0.19899   | -0.16817  | -0.22757              | -0.14502              | -0.07200       | -0.10359      | -0.07256      | -0.10359      | -0.10359      | -0.10359      | -0.10359      |
| $\bar{E}_{rm}$ (eV)                    | 0.11441    | 0.11441   | 0.14803   | 0.14803               | 0.14803               | 0.14803        | 0.14803       | 0.14803       | 0.14803       | 0.14803       | 0.14803       | 0.14803       |
| $E_{(w,m)}$ (eV)                       | -64.44771  | 32.76354  | -32.52811 | -67.92207             | -49.80996             | -31.70737      | -33.59732     | -33.59732     | -33.59732     | -33.59732     | -33.59732     | -33.59732     |
| $E_{(w,m)}$ (eV)                       | -14.63489  | -14.63489 | -14.63489 | -14.63489             | -14.63489             | -14.63489      | -14.63489     | -14.63489     | -14.63489     | -14.63489     | -14.63489     | -14.63489     |
| $E_{(w,m)}$ (eV)                       | 0          | 0         | 0         | -13.59844             | -13.59844             | -13.59844      | 0             | 0             | 0             | 0             | 0             | 0             |
| $E_{(w,m)}$ (eV)                       | 5.67933    | 3.49376   | 3.25833   | 12.49186              | 7.83016               | 3.37601        | 4.32754       | 4.29921       | 4.29921       | 4.17951       | 3.62128       | 3.91734       |

Table 15.199. The total bond energies of alkyl nitriles calculated using the functional group composition and the energies of Table 15.198 compared to the experimental values [3].

| Formula                         | NO Group | O-N Group | C-O Group | CH <sub>3</sub> Group | CH <sub>2</sub> Group | CH Group | C-C (a) Group | C-C (b) Group | C-C (c) Group | C-C (d) Group | C-C (e) Group | C-C (f) Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---------------------------------|----------|-----------|-----------|-----------------------|-----------------------|----------|---------------|---------------|---------------|---------------|---------------|---------------|-----------------------------------|-------------------------------------|----------------|
| CH <sub>3</sub> NO <sub>2</sub> | 1        | 1         | 1         | 1                     | 0                     | 0        | 0             | 0             | 0             | 0             | 0             | 0             | 24.9328                           | 24.955                              | 0.00126        |



# ALKYL NITRITES ( $C_nH_{2n+2-m}(NO_2)_m$ , $n = 1, 2, 3, 4, 5 \dots \infty$ )

The alkyl nitrites,  $C_nH_{2n+2-m}(NO_2)_m$ , comprise a  $RC-O-NO$  moiety that comprises  $C-O$ ,  $O-N$ , and  $NO$  functional groups. The alkyl portion of the alkyl nitrite may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise 5 methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, 10 and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in alkyl nitrites are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is  $1s^2 2s^2 2p^4$ , and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state  $^3P_2$ . The electron configuration of nitrogen is  $1s^2 2s^2 2p^3$ , and the orbital arrangement given by Eq. (10.134) has 15 three unpaired electrons corresponding to the ground state  $^4S_{3/2}^0$ . The bonding in the nitro ( $NO$ ) functional group is similar to that in the  $SO$  group given previously. It also has similarities to the bonding in the carbonyl functional group. In the  $NO$  group, the two unpaired electrons of the  $O$  atom form a MO with two unpaired electrons of the nitrogen atom such that the MO comprises a double bond. The nitrogen atom is then energy matched to the  $O-N$  functional 20 group that is further energy matched to the  $C2sp^3$  HO of the  $C-O$  functional group. To meet the equipotential condition of the union of the  $N=O$   $H_2$ -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor  $c_2$  of Eq. (15.51) for the  $N=O$ -bond MO given by Eq. (15.140) is  $c_2(O \text{ to } N2p \text{ to } C2sp^3HO) = 0.85987$ .

As in the case of the carbonyl group, two unpaired  $O$  electrons result upon bond 25 breakage of the  $N=O$  bond which requires that two times  $E_{mag}$  of oxygen (Eq. (15.59)) be subtracted from the total energy of  $NO$ . Additionally,  $E_r(atom - atom, msp^3.AO)$  and  $\Delta E_{H_1MO}(AO / HO)$  are equal to  $-0.92918 \text{ eV}$  (Eq. (14.513)) which matches the energy of the  $N=O$  bond with the contiguous  $O-N$  bond and matches the energy contribution of an oxygen atom.

The  $O-N$  functional group comprise a single-bond,  $H_2$ -type-ellipsoidal-MO between the remaining unpaired nitrogen electron and an unpaired electron of the second oxygen atom which further forms a single bond with the  $C2sp^3$  HO of the  $C-O$  functional group. In alkyl nitrites, the hybridization factor  $c_2$  of Eq. (15.52) for the  $C-O$ -bond MO given by Eq. 5 (15.114) is  $c_2(C2sp^3HO \text{ to } O) = 0.85395$ . The hybridization factor  $c_2$  of Eq. (15.52) for a  $C-N$ -bond MO given by Eq. (15.116) is  $c_2(C2sp^3HO \text{ to } N) = 0.91140$ . Thus, the hybridization factor  $c_2$  of Eq. (15.52) for  $O-N$  that bridges the  $C-O$  and  $N=O$  bonds given by Eq. (15.69) is

$$c_2(N2p \text{ to } O2p) = \frac{c_2(C2sp^3HO \text{ to } N)}{c_2(C2sp^3HO \text{ to } O)} = \frac{0.91140}{0.85395} = 1.06727 \quad (15.141)$$

10  $E_T(atom - atom, msp^3.AO) = -0.92918 \text{ eV}$  in order to match the energy of the  $NO$  group and  $E(AO / HO) = -15.35946 \text{ eV}$  in order to match the  $C-O$  functional group.

The  $C-O$  functional group is equivalent to that of an ether as given in the corresponding section except that  $E_T(atom - atom, msp^3.AO)$  and  $\Delta E_{H_2MO}(AO / HO)$  are both  $-0.72457 \text{ eV}$  which matches the energy contribution of an independent  $C2sp^3$  HO (Eq. 15 (14.151)). Also, the energy terms corresponding to the oscillation of the bond in the transition state are matched to a nitrite.

The symbols of the functional groups of branched-chain alkyl nitrites are given in Table 15.195. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl nitrites are given in Tables 20 15.196, 15.197, and 15.198, respectively. The total energy of each alkyl nitrite given in Table 15.199 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.198 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl nitrites determined using Eqs. (15.79-15.108) are given in Table 15.200.

Table 15.195. The symbols of functional groups of alkyl nitriles.

| Functional Group      | Group Symbol           |
|-----------------------|------------------------|
| NO group              | NO                     |
| O-N                   | O-N                    |
| C-O                   | C-O                    |
| CH <sub>3</sub> group | C-H (CH <sub>3</sub> ) |
| CH <sub>2</sub> group | C-H (CH <sub>2</sub> ) |
| CH                    | C-H                    |
| CC bond (n-C)         | C-C (a)                |
| CC bond (iso-C)       | C-C (b)                |
| CC bond (tert-C)      | C-C (c)                |
| CC (iso to iso-C)     | C-C (d)                |
| CC (t to t-C)         | C-C (e)                |
| CC (t to iso-C)       | C-C (f)                |

Table 15.196. The geometrical bond parameters of alkyl nitriles and experimental values [1].

| Parameter            | NO Group                                          | O-N Group                                           | C-O Group              | C-H (CH <sub>3</sub> ) Group              | C-H (CH <sub>2</sub> ) Group              | C-H Group         | C-C (a) Group                     | C-C (b) Group                     | C-C (c) Group                     | C-C (d) Group                     | C-C (e) Group                     | C-C (f) Group                     |
|----------------------|---------------------------------------------------|-----------------------------------------------------|------------------------|-------------------------------------------|-------------------------------------------|-------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| $a$ (Å)              | 1.32255                                           | 1.76440                                             | 1.85327                | 1.64920                                   | 1.67122                                   | 1.67465           | 2.12499                           | 2.12499                           | 2.10725                           | 2.12499                           | 2.10725                           | 2.10725                           |
| $c'$ (Å)             | 1.15002                                           | 1.52831                                             | 1.36135                | 1.04856                                   | 1.05553                                   | 1.05661           | 1.45744                           | 1.45744                           | 1.45164                           | 1.45744                           | 1.45164                           | 1.45164                           |
| Bond Length          |                                                   |                                                     |                        |                                           |                                           |                   |                                   |                                   |                                   |                                   |                                   |                                   |
| $2c'$ (Å)            | 1.21713                                           | 1.40582                                             | 1.44079                | 1.10974                                   | 1.11713                                   | 1.11827           | 1.54280                           | 1.54280                           | 1.53635                           | 1.54280                           | 1.53635                           | 1.53635                           |
| Exp. Bond Length (Å) | 1.205 (methyl nitrate)<br>1.2 (HNO <sub>2</sub> ) | 1.402 (methyl nitrate)<br>1.432 (HNO <sub>2</sub> ) | 1.437 (methyl nitrate) | 1.107 (C-H propane)<br>1.117 (C-H butane) | 1.107 (C-H propane)<br>1.117 (C-H butane) | 1.122 (isobutane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) |
| $h, c'$ (Å)          | 0.65314                                           | 1.16134                                             | 1.25751                | 1.27295                                   | 1.29569                                   | 1.29924           | 1.54616                           | 1.54616                           | 1.52750                           | 1.54616                           | 1.52750                           | 1.52750                           |
| $e$                  | 0.86955                                           | 0.75284                                             | 0.73457                | 0.63380                                   | 0.63159                                   | 0.63095           | 0.68600                           | 0.68600                           | 0.68888                           | 0.68600                           | 0.68888                           | 0.68888                           |

Table 15.197. The MO to HO intercept geometrical bond parameters of alkyl nitriles.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{mp}^2, \text{AO})$ .

| Bond                                                                         | Atom           | $E_T$<br>(eV)<br>Bond 1 | $E_T$<br>(eV)<br>Bond 2 | $E_T$<br>(eV)<br>Bond 3 | $E_T$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>( $\text{C}^2\text{sp}^3$ )<br>(eV) | $r_{\text{final}}$<br>( $a_0$ ) | $r_{\text{final}}$<br>( $a_0$ ) | $E_{\text{calculated}}$<br>(eV)<br>Final | $E(\text{C}^2\text{sp}^3)$<br>(eV)<br>Final | $\theta$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | $d_1$<br>( $a_0$ ) | $d_2$<br>( $a_0$ ) |
|------------------------------------------------------------------------------|----------------|-------------------------|-------------------------|-------------------------|-------------------------|--------------------------------------------------------------|---------------------------------|---------------------------------|------------------------------------------|---------------------------------------------|--------------------------|----------------------------|----------------------------|--------------------|--------------------|
| $\text{RON}=\text{O}$                                                        | O              | -0.46459                | 0                       | 0                       | 0                       |                                                              | 1.00000                         | 0.89943                         | -15.29034                                |                                             | 137.15                   | 42.85                      | 67.90                      | 0.9764             | 0.65238            |
| $\text{RON}=\text{O}$                                                        | N              | -0.46459                | -0.46459                | 0                       | 0                       |                                                              | 0.93084                         | 0.86359                         | -15.73493                                |                                             | 136.09                   | 43.91                      | 66.48                      | 0.9221             | 0.62221            |
| $\text{RON}=\text{NO}_2$                                                     | O <sub>2</sub> | -0.46459                | -0.36229                | 0                       | 0                       |                                                              | 1.00000                         | 0.86923                         | -15.63263                                |                                             | 99.22                    | 80.78                      | 47.63                      | 1.18005            | 0.19925            |
| $\text{RON}=\text{NO}_2$                                                     | N              | -0.46459                | -0.46459                | 0                       | 0                       |                                                              | 0.93084                         | 0.86359                         | -15.73493                                |                                             | 98.78                    | 81.22                      | 47.30                      | 1.19655            | 0.13175            |
| $\text{RH}_2\text{C}=\text{O}_2\text{NO}_2$                                  | O <sub>2</sub> | -0.36229                | -0.46459                | 0                       | 0                       |                                                              | 1.00000                         | 0.86923                         | -15.63263                                |                                             | 91.45                    | 88.57                      | 43.71                      | 1.33962            | 0.02173            |
| $\text{RH}_2\text{C}=\text{O}_2\text{NO}_2$                                  | N              | -0.36229                | 0                       | 0                       | 0                       |                                                              | 0.91771                         | 0.89582                         | -15.18804                                | -14.99717                                   | 93.71                    | 86.29                      | 45.31                      | 1.30342            | 0.05793            |
| $\text{CH}_2\text{H}_2\text{C}=\text{O}_2\text{NO}_2$                        | O <sub>2</sub> | -0.36229                | -0.92918                | 0                       | 0                       |                                                              | 0.91771                         | 0.84418                         | -16.11722                                | -15.92636                                   | 89.16                    | 90.84                      | 42.16                      | 1.37373            | 0.01238            |
| $\text{C}-\text{H}(\text{CH}_3)$                                             | C              | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                                   | 0.91771                         | 0.86359                         | -15.75493                                | -15.56407                                   | 77.49                    | 102.51                     | 41.48                      | 1.23564            | 0.18708            |
| $\text{C}-\text{H}(\text{CH}_3)$                                             | C              | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                                   | 0.91771                         | 0.81549                         | -16.68412                                | -16.49325                                   | 68.47                    | 111.53                     | 35.84                      | 1.35486            | 0.29933            |
| $\text{C}-\text{H}(\text{CH}_3)$                                             | C              | -0.92918                | -0.92918                | -0.92918                | 0                       | -154.40324                                                   | 0.91771                         | 0.77247                         | -17.61330                                | -17.42244                                   | 61.10                    | 118.90                     | 31.37                      | 1.42988            | 0.37326            |
| $\text{H}_3\text{C}_2\text{C}_2\text{H}_2\text{CH}_2-$<br>(C-C (a))          | C              | -0.92918                | 0                       | 0                       | 0                       | -152.54487                                                   | 0.91771                         | 0.86359                         | -15.75493                                | -15.56407                                   | 63.82                    | 116.18                     | 30.08                      | 1.83879            | 0.59106            |
| $\text{H}_3\text{C}_2\text{C}_2\text{H}_2\text{CH}_2-$<br>(C-C (b))          | C              | -0.92918                | -0.92918                | 0                       | 0                       | -153.47406                                                   | 0.91771                         | 0.81549                         | -16.68412                                | -16.49325                                   | 56.41                    | 123.59                     | 26.06                      | 1.90890            | 0.45117            |
| $\text{R}-\text{H}_2\text{C}_2\text{C}_2\text{H}_2\text{CH}_2-$<br>(C-C (a)) | C              | -0.92918                | -0.92918                | 0                       | 0                       | -154.40324                                                   | 0.91771                         | 0.77247                         | -17.61330                                | -17.42244                                   | 48.30                    | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| $\text{R}-\text{H}_2\text{C}_2\text{C}_2\text{H}_2\text{CH}_2-$<br>(C-C (b)) | C              | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -154.71860                                                   | 0.91771                         | 0.73889                         | -17.92866                                | -17.73779                                   | 48.21                    | 131.79                     | 21.74                      | 1.95734            | 0.50570            |
| $\text{R}-\text{H}_2\text{C}_2\text{C}_2\text{H}_2\text{CH}_2-$<br>(C-C (c)) | C              | -0.92918                | -0.72457                | -0.92918                | 0                       | -154.40324                                                   | 0.91771                         | 0.77247                         | -17.61330                                | -17.42244                                   | 48.30                    | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| $\text{R}-\text{H}_2\text{C}_2\text{C}_2\text{H}_2\text{CH}_2-$<br>(C-C (d)) | C              | -0.92918                | -0.72457                | -0.92918                | -0.72457                | -154.71860                                                   | 0.91771                         | 0.73889                         | -17.92866                                | -17.73779                                   | 50.04                    | 129.96                     | 22.66                      | 1.94462            | 0.49298            |
| $\text{R}-\text{H}_2\text{C}_2\text{C}_2\text{H}_2\text{CH}_2-$<br>(C-C (e)) | C              | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.11599                                                   | 0.91771                         | 0.76765                         | -17.92866                                | -17.73779                                   | 52.78                    | 127.22                     | 24.04                      | 1.92443            | 0.47279            |
| $\text{R}-\text{H}_2\text{C}_2\text{C}_2\text{H}_2\text{CH}_2-$<br>(C-C (f)) | C              | -0.72457                | -0.92918                | -0.92918                | 0                       | -154.19463                                                   | 0.91771                         | 0.78155                         | -17.40869                                | -17.21783                                   | 52.78                    | 127.22                     | 24.04                      | 1.92443            | 0.47279            |
| $\text{R}-\text{H}_2\text{C}_2\text{C}_2\text{H}_2\text{CH}_2-$<br>(C-C (g)) | C              | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -154.11599                                                   | 0.91771                         | 0.76765                         | -17.92866                                | -17.73779                                   | 50.04                    | 129.96                     | 22.66                      | 1.94462            | 0.49298            |



Table 15.198. The energy parameters (eV) of functional groups of alkyl nitriles.

| Parameters                                    | NO         | O-N       | C-O       | H <sub>2</sub> | H <sub>3</sub> | C-H            | C-C (a)   | C-C (b)   | C-C (c)   | C-C (d)   | C-C (e)   | C-C (f)   |
|-----------------------------------------------|------------|-----------|-----------|----------------|----------------|----------------|-----------|-----------|-----------|-----------|-----------|-----------|
| Group                                         | Group      | Group     | Group     | Group          | Group          | Group          | Group     | Group     | Group     | Group     | Group     | Group     |
| $n_1$                                         | 2          | 1         | 1         | 2              | 3              | 1              | 1         | 1         | 1         | 1         | 1         | 1         |
| $n_2$                                         | 0          | 0         | 0         | 2              | 2              | 0              | 0         | 0         | 0         | 0         | 0         | 0         |
| $n_3$                                         | 0          | 0         | 0         | 0              | 0              | 0              | 0         | 0         | 0         | 0         | 0         | 0         |
| $c_1$                                         | 0.5        | 0.5       | 0.5       | 0.75           | 0.75           | 0.75           | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       |
| $c_2$                                         | 1          | 1         | 1         | 1              | 1              | 1              | 1         | 1         | 1         | 1         | 1         | 1         |
| $c_3$                                         | 1          | 1         | 1         | 1              | 1              | 1              | 1         | 1         | 1         | 1         | 1         | 1         |
| $c_4$                                         | 0.85987    | 1.06727   | 0.85395   | 0.91771        | 0.91771        | 0.91771        | 0.91771   | 0.91771   | 0.91771   | 0.91771   | 0.91771   | 0.91771   |
| $c_5$                                         | 2          | 0         | 0         | 0              | 0              | 1              | 0         | 0         | 0         | 1         | 1         | 0         |
| $c_6$                                         | 4          | 2         | 2         | 1              | 1              | 1              | 2         | 2         | 2         | 2         | 2         | 2         |
| $c_7$                                         | 0          | 0         | 0         | 3              | 3              | 1              | 0         | 0         | 0         | 0         | 0         | 0         |
| $c_8$                                         | 0.5        | 0.5       | 0.5       | 0.75           | 0.75           | 0.75           | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       |
| $c_9$                                         | 1          | 1         | 1         | 1              | 1              | 1              | 1         | 1         | 1         | 1         | 1         | 1         |
| $c_{10}$                                      | -108.34117 | -42.83043 | -32.04173 | -107.32728     | -70.41425      | -35.12015      | -28.79214 | -28.79214 | -28.79214 | -28.79214 | -28.79214 | -29.10112 |
| $V_e$ (eV)                                    | 23.66182   | 20.48593  | 9.9436    | 38.92728       | 25.78002       | 12.87680       | 9.33532   | 9.33532   | 9.33532   | 9.33532   | 9.33532   | 9.37273   |
| $V_f$ (eV)                                    | 40.95920   | 12.13739  | 8.64465   | 32.53914       | 21.06675       | 10.48582       | 6.77464   | 6.77464   | 6.77464   | 6.77464   | 6.90500   | 6.90500   |
| $V_g$ (eV)                                    | -20.47960  | -6.06870  | -4.32232  | -16.26957      | -10.53537      | -5.24291       | -3.38732  | -3.38732  | -3.45250  | -3.38732  | -3.45250  | -3.45250  |
| $E_{\text{bond}}(e, \sigma, \pi)$ (eV)        | 0          | -15.35946 | -14.63489 | -15.56407      | -15.56407      | -14.63489      | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $\Delta E_{\text{bond}}(e, \sigma, \pi)$ (eV) | -0.92918   | 0         | -0.72457  | 0              | 0              | 0              | 0         | 0         | 0         | 0         | 0         | 0         |
| $E_{\text{bond}}(e, \sigma, \pi)$ (eV)        | 0.92918    | -15.35946 | -13.91032 | -15.56407      | -15.56407      | -14.63489      | -15.56407 | -15.56407 | -15.35946 | -15.56407 | -15.35946 | -15.35946 |
| $E_{\text{bond}}(e, \sigma, \pi)$ (eV)        | -63.27057  | -31.63537 | -31.63537 | -67.69451      | -49.66493      | -31.63533      | -31.63537 | -31.63537 | -31.63535 | -31.63537 | -31.63535 | -31.63535 |
| $E_{\text{bond}}(e, \sigma, \pi)$ (eV)        | -0.92918   | -0.92918  | -0.72457  | 0              | 0              | 0              | -1.85836  | -1.85836  | -1.44915  | -1.85836  | -1.44915  | -1.44915  |
| $E_{\text{bond}}(e, \sigma, \pi)$ (eV)        | -64.19992  | -32.56455 | -32.35994 | -67.69450      | -49.66493      | -31.63537      | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega$ ( $10^5 \text{ rad/s}$ )             | 19.2199    | 23.3578   | 20.7301   | 24.9286        | 24.2751        | 24.1759        | 9.43699   | 9.43699   | 15.4846   | 9.43699   | 9.55643   | 9.55643   |
| $E_{\text{bond}}(e, \sigma, \pi)$ (eV)        | 12.65089   | 15.37450  | 13.64490  | 16.40846       | 15.97831       | 15.91299       | 6.21159   | 6.21159   | 10.19220  | 6.21159   | 6.29021   | 6.29021   |
| $E_{\text{bond}}(e, \sigma, \pi)$ (eV)        | -0.22587   | 0.25261   | -0.25648  | -0.25352       | -0.25017       | -0.24966       | -0.16515  | -0.16515  | -0.20896  | -0.16515  | -0.16416  | -0.16416  |
| $E_{\text{bond}}(e, \sigma, \pi)$ (eV)        | 0.20396    | 0.10725   | 0.13663   | 0.35532        | 0.35532        | 0.35532        | 0.12312   | 0.12312   | 0.09944   | 0.12312   | 0.12312   | 0.12312   |
| $E_{\text{bond}}(e, \sigma, \pi)$ (eV)        | [46]       | [47]      | [21]      | (Eq. (13.458)) | (Eq. (13.458)) | (Eq. (13.458)) | [2]       | [4]       | [5]       | [2]       | [2]       | [2]       |
| $E_{\text{bond}}(e, \sigma, \pi)$ (eV)        | -0.12390   | 0.19899   | -0.16817  | -0.22757       | -0.14502       | -0.07200       | -0.10359  | -0.07526  | -0.13924  | -0.10359  | -0.10260  | -0.10260  |
| $E_{\text{bond}}(e, \sigma, \pi)$ (eV)        | 0.11441    | 0.11441   | 0.14803   | 0.14803        | 0.14803        | 0.14803        | 0.14803   | 0.14803   | 0.14803   | 0.14803   | 0.14803   | 0.14803   |
| $E_{\text{bond}}(e, \sigma, \pi)$ (eV)        | -64.44771  | 32.76354  | -32.52811 | -67.92207      | -49.80996      | -31.70737      | -33.59732 | -33.59732 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{\text{bond}}(e, \sigma, \pi)$ (eV)        | -14.63489  | -14.63489 | -14.63489 | -14.63489      | -14.63489      | -14.63489      | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{\text{bond}}(e, \sigma, \pi)$ (eV)        | 0          | 0         | 0         | -13.59844      | -13.59844      | -13.59844      | 0         | 0         | 0         | 0         | 0         | 0         |
| $E_{\text{bond}}(e, \sigma, \pi)$ (eV)        | 5.67933    | 3.49376   | 3.25833   | 12.49186       | 7.83016        | 3.32601        | 4.37754   | 4.29921   | 3.97398   | 4.17951   | 3.62128   | 3.91734   |

Table 15.199. The total bond energies of alkyl nitriles calculated using the functional group composition and the energies of Table 15.198 compared to the experimental values [3].

| Formula                         | Name           | NO | O-N | C-O | H <sub>2</sub> | H <sub>3</sub> | CH | C-H | C-C (a) | C-C (b) | C-C (c) | C-C (d) | C-C (e) | C-C (f) | Calculated Total Bond Energies (eV) | Experimental Total Bond Energies (eV) | Relative Error |
|---------------------------------|----------------|----|-----|-----|----------------|----------------|----|-----|---------|---------|---------|---------|---------|---------|-------------------------------------|---------------------------------------|----------------|
| CH <sub>3</sub> NO <sub>2</sub> | Methyl nitrite | 1  | 1   | 1   | 1              | 1              | 0  | 0   | 0       | 0       | 0       | 0       | 0       | 0       | 24.9328                             | 24.955                                | 0.00126        |

| Atoms of Angle                                       | $2c^1$<br>Bond 1<br>( $a_b$ ) | $2c^2$<br>Bond 2<br>( $a_b$ ) | $2c^3$<br>Terminal<br>Atoms ( $a_b$ ) | $F_1$ (eV) or<br>$E_1$ | Atom 1<br>Hybridization<br>Designation<br>(Table 15.3.A) | $E_{\text{orbital}}$<br>Atom 2 | Atom 2<br>Hybridization<br>Designation<br>(Table 15.3.A) | $c_2$<br>Atom 1 | $c_2$<br>Atom 2               | $C_1$ | $C_2$ | $c_1$ | $\zeta_2$ | $E_T$<br>(eV) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | Cal $\theta$<br>( $^\circ$ ) | Exp. $\theta$<br>( $^\circ$ ) |
|------------------------------------------------------|-------------------------------|-------------------------------|---------------------------------------|------------------------|----------------------------------------------------------|--------------------------------|----------------------------------------------------------|-----------------|-------------------------------|-------|-------|-------|-----------|---------------|----------------------------|----------------------------|------------------------------|-------------------------------|
| $\angle CO_N N$                                      | 2.72270                       | 2.65661                       | 4.4944                                | -16.68412<br>( $C_k$ ) | 25                                                       | -14.53414<br>( $N$ )           | N                                                        | 0.81549         | 0.91140<br>( $ES_k$ (15.116)) | I     | I     | I     | 0.86545   | -1.44915      |                            |                            | 113.33                       |                               |
| $\angle O_N MO_N$                                    | 2.30004                       | 2.65661                       | 4.1231                                | -16.68411<br>( $O_n$ ) | 24                                                       | -16.68411<br>( $O_k$ )         | 24                                                       | 0.81549         | 0.81549                       | I     | I     | I     | 0.81549   | -1.44915      |                            |                            | 112.38                       | 110.7<br>( $HNO_3$ )          |
| $\angle C_1 C_2 C_3$<br>Methylene<br>$\angle HC_1 H$ | 2.11106                       | 2.11106                       | 3.4252                                | -15.75493<br>( $C_k$ ) | 7                                                        | H                              | H                                                        | 0.86359         | I                             | I     | I     | 0.75  | 1.15796   | 0             |                            |                            | 108.44                       | 107<br>(propane)              |
| $\angle C_1 C_2 C_3$<br>Methyl<br>$\angle HC_1 H$    | 2.09711                       | 2.09711                       | 3.4252                                | -15.75493<br>( $C_k$ ) | 7                                                        | H                              | H                                                        | 0.86359         | I                             | I     | I     | 0.75  | 1.15796   | 0             |                            |                            | 109.50                       | 112<br>(propane)              |
| $\angle C_1 C_2 C_3$<br>Methyl<br>$\angle HC_1 H$    | 2.09711                       | 2.09711                       | 3.4252                                | -15.75493<br>( $C_k$ ) | 7                                                        | H                              | H                                                        | 0.86359         | I                             | I     | I     | 0.75  | 1.15796   | 0             |                            |                            | 109.44                       | 113.8<br>(butane)             |
| $\angle C_1 C_2 C_3$<br>Methyl<br>$\angle HC_1 H$    | 2.09711                       | 2.09711                       | 3.4252                                | -15.75493<br>( $C_k$ ) | 7                                                        | H                              | H                                                        | 0.86359         | I                             | I     | I     | 0.75  | 1.15796   | 0             |                            |                            | 109.44                       | 110.8<br>(isobutane)          |
| $\angle C_1 C_2 C_3$<br>Methyl<br>$\angle HC_1 H$    | 2.09711                       | 2.09711                       | 3.4252                                | -15.75493<br>( $C_k$ ) | 7                                                        | H                              | H                                                        | 0.86359         | I                             | I     | I     | 0.75  | 1.15796   | 0             |                            |                            | 109.44                       | 111.4<br>(isobutane)          |
| $\angle C_1 C_2 C_3$<br>Methyl<br>$\angle HC_1 H$    | 2.09711                       | 2.09711                       | 3.4252                                | -15.75493<br>( $C_k$ ) | 7                                                        | H                              | H                                                        | 0.86359         | I                             | I     | I     | 0.75  | 1.15796   | 0             |                            |                            | 109.44                       | 110.67<br>(isobutane)         |
| $\angle C_1 C_2 C_3$<br>Methyl<br>$\angle HC_1 H$    | 2.09711                       | 2.09711                       | 3.4252                                | -15.75493<br>( $C_k$ ) | 7                                                        | H                              | H                                                        | 0.86359         | I                             | I     | I     | 0.75  | 1.15796   | 0             |                            |                            | 109.44                       | 110.76                        |
| $\angle C_1 C_2 C_3$<br>Methyl<br>$\angle HC_1 H$    | 2.09711                       | 2.09711                       | 3.4252                                | -15.75493<br>( $C_k$ ) | 7                                                        | H                              | H                                                        | 0.86359         | I                             | I     | I     | 0.75  | 1.15796   | 0             |                            |                            | 109.44                       | 111.4<br>(isobutane)          |
| $\angle C_1 C_2 C_3$<br>Methyl<br>$\angle HC_1 H$    | 2.09711                       | 2.09711                       | 3.4252                                | -15.75493<br>( $C_k$ ) | 7                                                        | H                              | H                                                        | 0.86359         | I                             | I     | I     | 0.75  | 1.15796   | 0             |                            |                            | 109.44                       | 111.4<br>(isobutane)          |
| $\angle C_1 C_2 C_3$<br>Methyl<br>$\angle HC_1 H$    | 2.09711                       | 2.09711                       | 3.4252                                | -15.75493<br>( $C_k$ ) | 7                                                        | H                              | H                                                        | 0.86359         | I                             | I     | I     | 0.75  | 1.15796   | 0             |                            |                            | 109.44                       | 111.4<br>(isobutane)          |
| $\angle C_1 C_2 C_3$<br>Methyl<br>$\angle HC_1 H$    | 2.09711                       | 2.09711                       | 3.4252                                | -15.75493<br>( $C_k$ ) | 7                                                        | H                              | H                                                        | 0.86359         | I                             | I     | I     | 0.75  | 1.15796   | 0             |                            |                            | 109.44                       | 111.4<br>(isobutane)          |
| $\angle C_1 C_2 C_3$<br>Methyl<br>$\angle HC_1 H$    | 2.09711                       | 2.09711                       | 3.4252                                | -15.75493<br>( $C_k$ ) | 7                                                        | H                              | H                                                        | 0.86359         | I                             | I     | I     | 0.75  | 1.15796   | 0             |                            |                            | 109.44                       | 111.4<br>(isobutane)          |
| $\angle C_1 C_2 C_3$<br>Methyl<br>$\angle HC_1 H$    | 2.09711                       | 2.09711                       | 3.4252                                | -15.75493<br>( $C_k$ ) | 7                                                        | H                              | H                                                        | 0.86359         | I                             | I     | I     | 0.75  | 1.15796   | 0             |                            |                            | 109.44                       | 111.4<br>(isobutane)          |
| $\angle C_1 C_2 C_3$<br>Methyl<br>$\angle HC_1 H$    | 2.09711                       | 2.09711                       | 3.4252                                | -15.75493<br>( $C_k$ ) | 7                                                        | H                              | H                                                        | 0.86359         | I                             | I     | I     | 0.75  | 1.15796   | 0             |                            |                            | 109.44                       | 111.4<br>(isobutane)          |
| $\angle C_1 C_2 C_3$<br>Methyl<br>$\angle HC_1 H$    | 2.09711                       | 2.09711                       | 3.4252                                | -15.75493<br>( $C_k$ ) | 7                                                        | H                              | H                                                        | 0.86359         | I                             | I     | I     | 0.75  | 1.15796   | 0             |                            |                            | 109.44                       | 111.4<br>(isobutane)          |
| $\angle C_1 C_2 C_3$<br>Methyl<br>$\angle HC_1 H$    | 2.09711                       | 2.09711                       | 3.4252                                | -15.75493<br>( $C_k$ ) | 7                                                        | H                              | H                                                        | 0.86359         | I                             | I     | I     | 0.75  | 1.15796   | 0             |                            |                            | 109.44                       | 111.4<br>(isobutane)          |
| $\angle C_1 C_2 C_3$<br>Methyl<br>$\angle HC_1 H$    | 2                             |                               |                                       |                        |                                                          |                                |                                                          |                 |                               |       |       |       |           |               |                            |                            |                              |                               |

# ALKYL NITRATES ( $C_nH_{2n+2-m}(NO_2)_m$ , $n=1,2,3,4,5,\dots,\infty$ )

The alkyl nitrates,  $C_nH_{2n+2-m}(NO_2)_m$ , comprise a  $RC-O-NO_2$  moiety that comprises  $C-O$ ,  $O-N$ , and  $NO_2$  functional groups. The alkyl portion of the alkyl nitrate may comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups as well as  $C$  bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of  $C-C$  bonds can be identified. The n-alkane  $C-C$  bond is the same as that of straight-chain alkanes. In addition, the  $C-C$  bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl  $C-C$  bonds comprise functional groups. The branched-chain-alkane groups in alkyl nitrates are equivalent to those in branched-chain alkanes.

The  $NO_2$  functional group is equivalent to that of nitro alkanes with the exception that  $\Delta E_{H_2MO}(AO/HO)$  as well as  $E_T(atom-atom,msp^3.AO)$  is equal to  $-3.71673\text{ eV}$  in order to match the group energy to that of the contiguous  $O-N$  bond. Furthermore, the  $O-N$  group with  $E_T(atom-atom,msp^3.AO)=-0.92918\text{ eV}$  is equivalent to that of nitrites as given in the corresponding section.

The  $C-O$  functional group is equivalent to that of an ether as given in the corresponding section except that  $E_T(atom-atom,msp^3.AO)$  and  $\Delta E_{H_2MO}(AO/HO)$  are both  $-0.92918\text{ eV}$  which matches the energy contribution of an independent  $C2sp^3$  HO (Eq. (14.513)). Also, the energy terms corresponding to the oscillation of the bond in the transition state are matched to a nitrate.

The symbols of the functional groups of branched-chain alkyl nitrates are given in Table 15.201. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl nitrates are given in Tables 15.202, 15.203, and 15.204, respectively. The total energy of each alkyl nitrate given in Table 15.205 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.204 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl nitrates determined using Eqs. (15.79-15.108) are given in Table 15.206.

Table 15.201. The symbols of functional groups of alkyl nitrates.

| Functional Group      | Group Symbol           |
|-----------------------|------------------------|
| NO <sub>2</sub> group | NO <sub>2</sub>        |
| O-N                   | O-N                    |
| C-O                   | C-O                    |
| CH <sub>3</sub> group | C-H (CH <sub>3</sub> ) |
| CH <sub>2</sub> group | C-H (CH <sub>2</sub> ) |
| CH                    | C-H                    |
| CC bond (n-C)         | C-C (a)                |
| CC bond (iso-C)       | C-C (b)                |
| CC bond (tert-C)      | C-C (c)                |
| CC (iso to iso-C)     | C-C (d)                |
| CC (t to t-C)         | C-C (e)                |
| CC (t to iso-C)       | C-C (f)                |

Table 15.202. The geometrical bond parameters of alkyl nitrates and experimental values [1].

| Parameter               | NO <sub>2</sub> Group                             | O-N Group                                           | C-O Group              | C-H (CH <sub>3</sub> ) Group              | C-H (CH <sub>2</sub> ) Group              | C-H Group         | C-C (a) Group                     | C-C (b) Group                     | C-C (c) Group                     | C-C (d) Group                     | C-C (e) Group                     | C-C (f) Group                     |
|-------------------------|---------------------------------------------------|-----------------------------------------------------|------------------------|-------------------------------------------|-------------------------------------------|-------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| $\alpha$ (°)            | 1.29538                                           | 1.76440                                             | 1.83991                | 1.64920                                   | 1.67122                                   | 1.67465           | 2.12499                           | 2.12499                           | 2.10725                           | 2.12499                           | 2.10725                           | 2.10725                           |
| $c'$ (°)                | 1.13815                                           | 1.32831                                             | 1.35643                | 1.04856                                   | 1.05553                                   | 1.05661           | 1.45744                           | 1.45744                           | 1.45164                           | 1.45744                           | 1.45164                           | 1.45164                           |
| Bond Length<br>2c' (Å)  | 1.20456                                           | 1.40582                                             | 1.43559                | 1.10974                                   | 1.11713                                   | 1.11827           | 1.54280                           | 1.54280                           | 1.53635                           | 1.54280                           | 1.53635                           | 1.53635                           |
| Exp. Bond Length<br>(Å) | 1.205 (methyl nitrate)<br>1.2 (HNO <sub>2</sub> ) | 1.402 (methyl nitrate)<br>1.432 (HNO <sub>2</sub> ) | 1.437 (methyl nitrate) | 1.107 (C-H propane)<br>1.117 (C-H butane) | 1.107 (C-H propane)<br>1.117 (C-H butane) | 1.122 (isobutane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) | 1.532 (propane)<br>1.531 (butane) |
| $h,c$ (°)               | 0.61857                                           | 1.16134                                             | 1.24312                | 1.27295                                   | 1.29569                                   | 1.29924           | 1.54616                           | 1.54616                           | 1.52750                           | 1.54616                           | 1.52750                           | 1.52750                           |
| $e$                     | 0.87862                                           | 0.75284                                             | 0.73723                | 0.63580                                   | 0.63159                                   | 0.63095           | 0.68600                           | 0.68600                           | 0.68888                           | 0.68600                           | 0.68888                           | 0.68888                           |

Table 15.203. The MO to HO intercept geometrical bond parameters of alkyl nitrates.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{mwp}, \text{AO})$ .

| Bond                             | Atom            | $E_T$<br>(eV)<br>Bond 1 | $E_T$<br>(eV)<br>Bond 2 | $E_T$<br>(eV)<br>Bond 3 | $E_T$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>$C_{2sp^2}$<br>(eV) | $r_{\text{final}}$<br>( $a_0$ ) | $r_{\text{final}}$<br>( $a_0$ ) | $E(\text{Final})$<br>(eV) | $\theta$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | $d_1$<br>( $a_0$ ) | $d_2$<br>( $a_0$ ) |
|----------------------------------|-----------------|-------------------------|-------------------------|-------------------------|-------------------------|----------------------------------------------|---------------------------------|---------------------------------|---------------------------|--------------------------|----------------------------|----------------------------|--------------------|--------------------|
| $RN(O)=O$                        | O               | -0.92918                | 0                       | 0                       | 0                       | -15.75493                                    | 0.86359                         | 0.86359                         | -15.75493                 | 138.49                   | 41.51                      | 67.70                      | 0.49144            | 0.64071            |
| $RN(O)=O$                        | N               | -0.92918                | -0.92918                | -0.46459                | 0                       | -17.14870                                    | 0.79540                         | 0.79540                         | -17.14870                 | 135.60                   | 44.40                      | 63.83                      | 0.37133            | 0.56082            |
| $RO_2-N(O)_2$                    | O <sub>1a</sub> | -0.46459                | -0.46459                | 0                       | 0                       | -15.75493                                    | 0.86359                         | 0.86359                         | -15.75493                 | 98.78                    | 81.22                      | 47.30                      | 1.19635            | 0.13175            |
| $RO_2-N(O)_2$                    | N               | -0.46459                | -0.92918                | -0.92918                | 0                       | -17.14870                                    | 0.79540                         | 0.79540                         | -17.14870                 | 92.78                    | 87.22                      | 43.03                      | 1.28978            | 0.03852            |
| $RH_2C_2-O_2N(O)_2$              | O <sub>1a</sub> | -0.46459                | -0.46459                | 0                       | 0                       | -15.75493                                    | 0.86359                         | 0.86359                         | -15.75493                 | 92.13                    | 87.87                      | 43.96                      | 1.32431            | 0.03212            |
| $R=H, \text{ allyl}$             | C <sub>1a</sub> | -0.46459                | 0                       | 0                       | 0                       | -15.20934                                    | 0.88983                         | 0.88983                         | -15.20934                 | 94.36                    | 85.64                      | 45.54                      | 1.28972            | 0.06771            |
| $-CH_2H_2C_2-O_2N(O)_2$          | C <sub>1a</sub> | -0.46459                | -0.92918                | 0                       | 0                       | -16.21952                                    | 0.83885                         | 0.83885                         | -16.21952                 | 89.90                    | 90.10                      | 42.44                      | 1.35787            | 0.00143            |
| $C-H (CH_2)$                     | C <sub>1</sub>  | -0.92918                | 0                       | 0                       | 0                       | -15.54487                                    | 0.91771                         | 0.86359                         | -15.54407                 | 77.49                    | 102.51                     | 41.48                      | 1.23564            | 0.18708            |
| $C-H (CH_2)$                     | C <sub>1</sub>  | -0.92918                | -0.92918                | 0                       | 0                       | -16.68412                                    | 0.81549                         | 0.81549                         | -16.68412                 | 68.47                    | 111.53                     | 35.84                      | 1.35486            | 0.29933            |
| $C-H (CH)$                       | C <sub>1</sub>  | -0.92918                | -0.92918                | -0.92918                | 0                       | -17.42244                                    | 0.77247                         | 0.77247                         | -17.42244                 | 61.10                    | 118.90                     | 31.37                      | 1.42988            | 0.37326            |
| $H_2C_2H_2CH_2-$<br>(C-C (a))    | C <sub>1a</sub> | -0.92918                | 0                       | 0                       | 0                       | -15.75493                                    | 0.86359                         | 0.86359                         | -15.75493                 | 63.82                    | 116.18                     | 30.08                      | 1.83879            | 0.38106            |
| $H_2C_2H_2CH_2-$<br>(C-C (a))    | C <sub>1a</sub> | -0.92918                | -0.92918                | 0                       | 0                       | -16.68412                                    | 0.81549                         | 0.81549                         | -16.68412                 | 56.41                    | 123.59                     | 26.06                      | 1.90890            | 0.45117            |
| $R-H_2C_2H_2CH_2-$<br>(C-C (b))  | C <sub>1a</sub> | -0.92918                | -0.92918                | -0.92918                | 0                       | -17.61330                                    | 0.77247                         | 0.77247                         | -17.61330                 | 48.30                    | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| $R-H_2C_2H_2CH_2-$<br>(C-C (c))  | C <sub>1a</sub> | -0.92918                | -0.72457                | -0.72457                | -0.72457                | -15.71860                                    | 0.75889                         | 0.75889                         | -17.92866                 | 48.21                    | 131.79                     | 21.74                      | 1.95734            | 0.50570            |
| $R_2O_2C_2H_2CH_2-$<br>(C-C (d)) | C <sub>1a</sub> | -0.92918                | -0.92918                | -0.92918                | 0                       | -15.40324                                    | 0.91771                         | 0.77247                         | -17.42244                 | 48.30                    | 131.70                     | 21.90                      | 1.97162            | 0.51388            |
| $R_2O_2C_2H_2CH_2-$<br>(C-C (e)) | C <sub>1a</sub> | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -15.451399                                   | 0.91771                         | 0.76765                         | -17.92866                 | 50.04                    | 129.96                     | 22.66                      | 1.94462            | 0.49298            |
| $R_2O_2C_2H_2CH_2-$<br>(C-C (f)) | C <sub>1a</sub> | -0.72457                | -0.92918                | -0.92918                | 0                       | -15.419863                                   | 0.91771                         | 0.78155                         | -17.40869                 | 52.78                    | 127.22                     | 24.04                      | 1.92443            | 0.47279            |
| $R_2O_2C_2H_2CH_2-$<br>(C-C (g)) | C <sub>1a</sub> | -0.72457                | -0.72457                | -0.72457                | -0.72457                | -15.451399                                   | 0.91771                         | 0.76765                         | -17.92866                 | 50.04                    | 129.96                     | 22.66                      | 1.94462            | 0.49298            |

Table 15.204. The energy parameters (eV) of functional groups of alkyl nitrates.

| Parameters                          | $\text{NO}_2^-$ | O-N       | C-O       | $\text{CH}_3$       | $\text{CH}_2$       | C-H                 | C-C (a)   | C-C (b)   | C-C (c)   | C-C (d)   | C-C (e)   | C-C (f)   |
|-------------------------------------|-----------------|-----------|-----------|---------------------|---------------------|---------------------|-----------|-----------|-----------|-----------|-----------|-----------|
| Group                               | Group           | Group     | Group     | Group               | Group               | Group               | Group     | Group     | Group     | Group     | Group     | Group     |
| $n_1$                               | 2               | 1         | 1         | 3                   | 2                   | 1                   | 1         | 1         | 1         | 1         | 1         | 1         |
| $n_2$                               | 0               | 0         | 0         | 2                   | 1                   | 0                   | 0         | 0         | 0         | 0         | 0         | 0         |
| $n_3$                               | 0               | 0         | 0         | 0                   | 0                   | 0                   | 0         | 0         | 0         | 0         | 0         | 0         |
| $C_1$                               | 0.5             | 0.5       | 0.5       | 0.75                | 0.75                | 0.75                | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       |
| $C_2$                               | 1               | 1         | 1         | 1                   | 1                   | 1                   | 1         | 1         | 1         | 1         | 1         | 1         |
| $C_3$                               | 1               | 1         | 1         | 1                   | 1                   | 1                   | 1         | 1         | 1         | 1         | 1         | 1         |
| $C_4$                               | 0.85987         | 1.06727   | 0.85593   | 0.91771             | 0.91771             | 0.91771             | 0.91771   | 0.91771   | 0.91771   | 0.91771   | 0.91771   | 0.91771   |
| $C_5$                               | 0               | 0         | 0         | 0                   | 1                   | 1                   | 0         | 0         | 0         | 1         | 1         | 0         |
| $C_6$                               | 4               | 2         | 2         | 1                   | 1                   | 1                   | 2         | 2         | 2         | 2         | 2         | 2         |
| $C_7$                               | 0               | 0         | 0         | 3                   | 2                   | 1                   | 0         | 0         | 0         | 0         | 0         | 0         |
| $C_8$                               | 0.5             | 0.5       | 0.5       | 0.75                | 0.75                | 0.75                | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       |
| $C_9$                               | 1               | 1         | 1         | 1                   | 1                   | 1                   | 1         | 1         | 1         | 1         | 1         | 1         |
| $F_1$ (eV)                          | -112.63415      | -42.85043 | -32.35681 | -107.32728          | -70.41425           | -35.12015           | -28.79214 | -28.79214 | -29.10112 | -28.79214 | -29.10112 | -29.10112 |
| $F_2$ (eV)                          | 23.90868        | 20.48593  | 10.03058  | 38.92728            | 25.78002            | 12.87680            | 9.3352    | 9.3352    | 9.3352    | 9.3352    | 9.3352    | 9.3352    |
| $F_3$ (eV)                          | 43.47534        | 12.13759  | 8.79504   | 32.53914            | 21.06675            | 10.48582            | 6.77464   | 6.77464   | 6.90500   | 6.77464   | 6.90500   | 6.90500   |
| $F_4$ (eV)                          | -21.75767       | -6.66870  | -4.59652  | -16.26957           | -10.55337           | -5.34291            | -3.38732  | -3.38732  | -3.45250  | -3.38732  | -3.45250  | -3.45250  |
| $E_{1,2,3,4,5,6,7,8,9}$ (eV)        | 0               | -15.35946 | -14.63489 | -15.56407           | -15.56407           | -14.63489           | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 |
| $\Delta E_{1,2,3,4,5,6,7,8,9}$ (eV) | -3.71673        | 0         | -0.92918  | 0                   | 0                   | 0                   | 0         | 0         | 0         | 0         | 0         | 0         |
| $E_{1,2,3,4,5,6,7,8,9}$ (eV)        | 3.71673         | -15.35946 | -13.70571 | -15.56407           | -15.56407           | -14.63489           | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 | -15.56407 |
| $E_{1,2,3,4,5,6,7,8,9}$ (eV)        | -63.27107       | -31.63527 | -31.63542 | -67.69451           | -49.66493           | -31.63533           | -31.63537 | -31.63537 | -31.63537 | -31.63537 | -31.63537 | -31.63537 |
| $E_{1,2,3,4,5,6,7,8,9}$ (eV)        | -3.71673        | -0.92918  | -0.92918  | 0                   | 0                   | 0                   | -1.85836  | -1.85836  | -1.44915  | -1.85836  | -1.44915  | -1.44915  |
| $E_{1,2,3,4,5,6,7,8,9}$ (eV)        | -66.98746       | -32.56455 | -32.56455 | -67.69450           | -49.66493           | -31.63537           | -33.49373 | -33.49373 | -33.08452 | -33.49373 | -33.08452 | -33.08452 |
| $\omega$ ( $10^{15}$ rad/s)         | 19.8278         | 23.3578   | 21.0910   | 24.9286             | 24.2751             | 24.1759             | 9.43699   | 9.43699   | 9.43699   | 9.43699   | 9.43699   | 9.43699   |
| $E_{1,2,3,4,5,6,7,8,9}$ (eV)        | 13.05099        | 15.37450  | 13.88249  | 16.40846            | 15.97831            | 15.91299            | 6.21159   | 6.21159   | 6.21159   | 6.21159   | 6.21159   | 6.21159   |
| $E_{1,2,3,4,5,6,7,8,9}$ (eV)        | -0.23938        | 0.25261   | -0.24004  | -0.25352            | -0.25017            | -0.24966            | -0.16515  | -0.16515  | -0.20896  | -0.16515  | -0.16416  | -0.16416  |
| $E_{1,2,3,4,5,6,7,8,9}$ (eV)        | 0.19342         | 0.10725   | 0.13663   | 0.35532             | 0.35532             | 0.35532             | 0.12312   | 0.12312   | 0.09944   | 0.12312   | 0.12312   | 0.12312   |
| $E_{1,2,3,4,5,6,7,8,9}$ (eV)        | [45]            | [47]      | [21]      | ( $E_0$ , (13.458)) | ( $E_0$ , (13.458)) | ( $E_0$ , (13.458)) | [2]       | [4]       | [5]       | [2]       | [2]       | [2]       |
| $E_{1,2,3,4,5,6,7,8,9}$ (eV)        | -0.14267        | 0.19899   | -0.17172  | -0.22757            | -0.14502            | -0.07200            | -0.10359  | -0.07526  | -0.15924  | -0.10359  | -0.10260  | -0.10260  |
| $E_{1,2,3,4,5,6,7,8,9}$ (eV)        | 0.11441         | 0.11441   | 0.14803   | 0.14803             | 0.14803             | 0.14803             | 0.14803   | 0.14803   | 0.14803   | 0.14803   | 0.14803   | 0.14803   |
| $E_{1,2,3,4,5,6,7,8,9}$ (eV)        | -67.27281       | 32.76554  | -32.73627 | -67.92207           | -49.80996           | -31.70737           | -33.59732 | -33.59732 | -33.24376 | -33.59732 | -33.18712 | -33.18712 |
| $E_{1,2,3,4,5,6,7,8,9}$ (eV)        | -14.63489       | -14.63489 | -14.63489 | -14.63489           | -14.63489           | -14.63489           | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 | -14.63489 |
| $E_{1,2,3,4,5,6,7,8,9}$ (eV)        | 0               | 0         | 0         | -13.59844           | -13.59844           | -13.59844           | 0         | 0         | 0         | 0         | 0         | 0         |
| $E_{1,2,3,4,5,6,7,8,9}$ (eV)        | 8.73325         | 3.49376   | 3.46649   | 12.49186            | 7.83016             | 3.32601             | 4.32754   | 4.29921   | 3.97398   | 4.17951   | 3.62128   | 3.91734   |

Table 15.205. The total bond energies of alkyl nitrates calculated using the functional group composition and the energies of Table 15.204 compared to the experimental values [3].

| Formula                           | Name              | $\text{NO}_2^-$ | O-N | C-O | $\text{CH}_3$ | $\text{CH}_2$ | C-H | C-C (a) | C-C (b) | C-C (c) | C-C (d) | C-C (e) | C-C (f) | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|-----------------------------------|-------------------|-----------------|-----|-----|---------------|---------------|-----|---------|---------|---------|---------|---------|---------|-----------------------------------|-------------------------------------|----------------|
| $\text{CH}_3\text{NO}_2$          | Methyl nitrate    | 1               | 1   | 1   | 1             | 0             | 0   | 0       | 0       | 0       | 0       | 0       | 0       | 38.117                            | 38.117                              | -0.00244       |
| $\text{C}_2\text{H}_5\text{NO}_2$ | Ethyl nitrate     | 1               | 1   | 1   | 1             | 1             | 0   | 0       | 0       | 0       | 0       | 0       | 0       | 40.386                            | 40.386                              | 0.00151        |
| $\text{C}_3\text{H}_7\text{NO}_2$ | Propyl nitrate    | 1               | 1   | 1   | 1             | 2             | 0   | 0       | 0       | 0       | 0       | 0       | 0       | 52.5076                           | 52.5076                             | 0.00053        |
| $\text{C}_4\text{H}_9\text{NO}_2$ | Isopropyl nitrate | 1               | 1   | 1   | 2             | 0             | 1   | 0       | 2       | 0       | 0       | 0       | 0       | 52.60168                          | 52.725                              | 0.00233        |

Table 15.206. The bond angle parameters of alkyl nitrates and experimental values [1]. In the calculation of  $\theta_e$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{msp}^3 \text{AO})$ .

| Atoms of angle                            | $2c_1^*$<br>Bond 1<br>( $a_0$ ) | $2c_2^*$<br>Bond 2<br>( $a_0$ ) | $2c_3^*$<br>Terminal<br>Atom<br>( $a_0$ ) | $E_{\text{terminal}}$<br>or<br>$E$<br>Atom 1 | Atom 1<br>Hybridization<br>Designation<br>(Table 15.3.A) | $c_2$<br>Atom 1 | $c_2$<br>Atom 2<br>(Eq. 15.14.4) | $c_1$   | $c_2^*$ | $E_T$<br>(eV) | $\theta_e$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | Cal. $\theta$<br>( $^\circ$ ) | Exp. $\theta$<br>( $^\circ$ )                                 |
|-------------------------------------------|---------------------------------|---------------------------------|-------------------------------------------|----------------------------------------------|----------------------------------------------------------|-----------------|----------------------------------|---------|---------|---------------|----------------------------|----------------------------|----------------------------|-------------------------------|---------------------------------------------------------------|
| $\angle \text{H}_c \text{C}_a \text{H}_b$ | 2.09711                         | 2.09711                         | 3.4252                                    | -15.75493                                    | 7                                                        | H               |                                  | 0.86359 | I       | 0             |                            |                            |                            | 109.50                        |                                                               |
| $\angle \text{H}_c \text{C}_a \text{O}_b$ |                                 |                                 |                                           |                                              |                                                          |                 |                                  |         |         |               | 70.56                      |                            |                            | 109.44                        | 110<br>(methyl nitrate)                                       |
| $\angle \text{H}_c \text{C}_a \text{O}_b$ | 2.09711                         | 2.71287                         | 3.7238                                    | -14.82575<br>$C_a$                           | I                                                        |                 | 0.83595<br>(Eq. 15.14.4)         | 0.75    | 0.93852 | 0             |                            |                            |                            | 100.68                        | 103<br>(methyl nitrate)                                       |
| $\angle \text{O}_a \text{NO}_b$           | 2.27630                         | 2.27630                         | 4.1231                                    | -16.68411<br>$O_a$                           | 24                                                       |                 | 0.81549                          | I       | 0.81549 | -1.44915      |                            |                            |                            | 129.83                        |                                                               |
| $\angle \text{O}_a \text{NO}_b$           |                                 |                                 |                                           |                                              |                                                          |                 |                                  |         |         |               |                            | 129.83                     |                            | 115.09<br>(Eq. 15.59)         | 118.1<br>(methyl nitrate)                                     |
| $\angle \text{O}_a \text{NO}_b$           |                                 |                                 |                                           |                                              |                                                          |                 |                                  |         |         |               |                            | 129.83                     |                            | 115.09<br>(Eq. 15.59)         | 112.4<br>(methyl nitrate)                                     |
| $\angle \text{O}_a \text{NO}_b$           | 2.71287                         | 2.65661                         | 4.4721                                    | -16.68412<br>$C_a$                           | 25                                                       | N               | 0.91140<br>(Eq. 15.11.6)         | I       | 0.86345 | -1.44915      |                            |                            |                            | 112.79                        | 112.7<br>(methyl nitrate)                                     |
| $\angle \text{H}_c \text{C}_a \text{H}_b$ | 2.11106                         | 2.11106                         | 3.4252                                    | -15.75493                                    | 7                                                        | H               |                                  | 0.86359 | I       | 0             |                            |                            |                            | 108.44                        | 107<br>(propane)                                              |
| $\angle \text{C}_a \text{C}_b \text{C}_c$ |                                 |                                 |                                           |                                              |                                                          |                 |                                  |         |         |               | 69.51                      |                            |                            | 110.49                        | 112<br>(propane)<br>113.8<br>(butane)<br>116.8<br>(isobutane) |
| $\angle \text{C}_a \text{C}_b \text{H}_c$ |                                 |                                 |                                           |                                              |                                                          |                 |                                  |         |         |               |                            | 69.51                      |                            | 110.49                        | 111.0<br>(butane)<br>111.4<br>(isobutane)                     |
| $\angle \text{H}_c \text{C}_a \text{H}_b$ | 2.09711                         | 2.09711                         | 3.4252                                    | -15.75493                                    | 7                                                        | H               |                                  | 0.86359 | I       | 0             |                            |                            |                            | 109.50                        |                                                               |
| $\angle \text{C}_a \text{C}_b \text{C}_c$ |                                 |                                 |                                           |                                              |                                                          |                 |                                  |         |         |               | 70.56                      |                            |                            | 109.44                        |                                                               |
| $\angle \text{C}_a \text{C}_b \text{H}_c$ |                                 |                                 |                                           |                                              |                                                          |                 |                                  |         |         |               | 70.56                      |                            |                            | 109.44                        |                                                               |
| $\angle \text{C}_a \text{C}_b \text{C}_c$ | 2.91547                         | 2.91547                         | 4.7958                                    | -16.68412<br>$C_a$                           | 25                                                       |                 | 0.81549                          | I       | 0.81549 | -1.85836      |                            |                            |                            | 110.67                        | 110.8<br>(isobutane)                                          |
| $\angle \text{C}_a \text{C}_b \text{H}_c$ | 2.91547                         | 2.11323                         | 4.1633                                    | -15.50033<br>$C_a$                           | 5                                                        | I               | 0.87495                          | 0.91771 | 1.04887 | 0             |                            |                            |                            | 110.76                        |                                                               |
| $\angle \text{C}_a \text{C}_b \text{H}_c$ | 2.91547                         | 2.09711                         | 4.1633                                    | -15.50033<br>$C_a$                           | 5                                                        | I               | 0.87495                          | 0.91771 | 1.04887 | 0             |                            |                            |                            | 111.27                        | 111.4<br>(isobutane)                                          |
| $\angle \text{C}_a \text{C}_b \text{C}_c$ | 2.90327                         | 2.90327                         | 4.7958                                    | -15.50033<br>$C_a$                           | 5                                                        | I               | 0.87495                          | 0.91771 | 1.04887 | -1.85836      |                            |                            |                            | 111.27                        | 111.4<br>(isobutane)                                          |
| $\angle \text{C}_a \text{C}_b \text{C}_c$ |                                 |                                 |                                           |                                              |                                                          |                 |                                  |         |         |               | 72.50                      |                            |                            | 107.50                        |                                                               |

## CYCLIC AND CONJUGATED ALKENES

$$(C_n H_{2n+2-2m-2c}, \quad n=3,4,5\ldots\infty, \quad m=1,2,3\ldots, \quad c=0 \text{ or } 1)$$

The cyclic and conjugated alkenes are represented by the general formula  $C_n H_{2n+2-2m-2c}$ ,  $n=3,4,5\ldots\infty$ ,  $m=1,2,3\ldots$ ,  $c=0$  or  $1$  where  $m$  is the number of double bonds and  $c=0$  for a straight-chain alkene and  $c=1$  for a cyclic alkene. They have at least one carbon-carbon double bond comprising a functional group that is solved equivalently to the double bond of ethylene. Consider the cyclic and conjugated alkenes 1,3-butadiene, 1,3-pentadiene, 1,4-pentadiene, 1,3-cyclopentadiene, and cyclopentene. Based on the condition of energy matching of the orbital, any magnetic energy due to unpaired electrons in the constituent fragments, and differences in oscillation in the transition state, five distinct  $C-C$  functional groups can be identified as given in Table 15.208. The designation of the structure of the groups are shown in Figures 61A-E. In addition,  $CH_2$  of any  $-C=CH_2$  moiety is an conjugated alkene functional group. The alkyl portion of the cyclic or conjugated alkene may comprise at least one terminal methyl group ( $CH_3$ ), and may comprise methylene ( $CH_2$ ), and methylene ( $CH$ ) functional groups that are equivalent to those of branched-chain alkanes.

The solution of the functional groups comprises the hybridization of the  $2s$  and  $2p$  AOs of each  $C$  to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. The  $C-C$  groups are solved in the same manner as those of the branched-chain alkanes given in the corresponding section. For example, the cyclopentene  $C_a-C_b$  group is equivalent to the  $n-C-C$  alkane group. Many of the corresponding energies of the molecules of this class are similar, and they can be related to one another based on the structure. For example, cyclopentadiene is formed by ring closure of 1,3-pentadiene with the elimination of  $H$  from the terminal methyl and methylene groups. Thus, the energy of each of the corresponding carbon-carbon bonds in cyclopentadiene is the same as that in 1,3-pentadiene except that the difference between the energies of the 1,3-pentadiene  $C_c-C_d$  and the cyclopentadiene  $C_a-C_b$  groups is the magnetic energy (Eq. (15.58)) which is subtracted from the  $C_a-C_b$  total bond energy according to Eqs. (13.524-13.527) due to the formation of a  $CH$  group from the methylene group.

$E_T(atom-atom,msp^3.AO)$  of the  $C=C$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  atoms to the MO is equivalent to that of ethylene,  $-2.26759 \text{ eV}$ , given by



Eq. (14.247).  $E_r(\text{atom} - \text{atom}, msp^3.AO)$  of each  $C - C$ -bond MO in Eq. (15.52) is  $-2.26759 \text{ eV}$  or  $-1.85836 \text{ eV}$  based on the energy match between the  $C2sp^3$  HOs corresponding to the energy contributions equivalent to those of alkene,  $-1.13379 \text{ eV}$  (Eq. (14.247)), or methylene,  $-0.92918 \text{ eV}$  (Eq. (14.513)), groups, respectively, that are contiguous  
 5 with the  $C - C$ -bond carbons. In the former case, the total energy of the  $C - C$  bond MO is matched to that of the alkane energy in the determination of the bond length. The charge density of  $0.5e$  must be donated to the  $C - C$  bond in order to match the energy of the adjacent flanking double bonds. This further lowers the total energy of the  $C - C$ -bond MO and increases the  $C - C$  bond energy. This additional lowering of the  $C - C$ -bond energy by additional charge  
 10 donation over that of an alkane bond due to adjacent double bonds is called *conjugation*.

The symbols of the functional groups of cyclic and conjugated alkenes are given in Table 15.207. The structures of 1,3-butadiene, 1,3-pentadiene, 1,4-pentadiene, 1,3-cyclopentadiene, and cyclopentene are shown in Figures 61A-E, respectively. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56))  
 15 parameters of cyclic and conjugated alkenes are given in Tables 15.208, 15.209, and 15.210, respectively. The total energy of each cyclic or conjugated alkenes given in Table 15.211 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.210 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum  
 20 of the  $E_D(\text{group})$  ( $\text{eV}$ ) values based on composition is given by Eq. (15.58). The bond angle parameters of cyclic and conjugated alkenes determined using Eqs. (15.79-15.108) are given in Table 15.212.

Table 15.207. The symbols of functional groups of cyclic and conjugated alkenes.

| Functional Group                        | Group Symbol       |
|-----------------------------------------|--------------------|
| CC double bond                          | C=C                |
| 1,3-butadiene, 1,3-pentadiene $C_s-C_s$ | $C'-C' (a)$        |
| 1,3-cyclopentadiene $C_s-C_s$           | $C'-C' (a)$        |
| 1,3-pentadiene $C_s-C_s$                | $C'-C' (b)$        |
| cyclopentene $C_s-C_s$                  | $C'-C' (b)$        |
| 1,4-pentadiene $C_s-C_s$                | $C'-C' (c)$        |
| 1,3-cyclopentadiene $C_s-C_s$           | $C'-C' (d)$        |
| cyclopentene $C_s-C_s$                  | $C'-C' (e)$        |
| CH <sub>2</sub> alkyl group             | $C'-H (CH_2) (i)$  |
| CH <sub>3</sub> group                   | $C'-H (CH_3)$      |
| CH <sub>3</sub> alkyl group             | $C'-H (CH_2) (ii)$ |
| CH                                      | $C'-H$             |

Table 15.208. The geometrical bond parameters of cyclic and conjugated alkenes and experimental values [1].

| Parameter              | C=C Group                                                                                                   | $C'-C' (a)$ Group                                    | $C'-C' (b)$ Group    | $C'-C' (c)$ Group           | $C'-C' (d)$ Group           | $C'-C' (e)$ Group    | $C-H (CH_2) (i)$ Group                                           | $C-H (CH_2) (ii)$ Group                   | C-H Group         |
|------------------------|-------------------------------------------------------------------------------------------------------------|------------------------------------------------------|----------------------|-----------------------------|-----------------------------|----------------------|------------------------------------------------------------------|-------------------------------------------|-------------------|
| $a (a_e)$              | 1.47228                                                                                                     | 1.91256                                              | 2.04740              | 2.04740                     | 2.04740                     | 2.04740              | 1.64010                                                          | 1.67122                                   | 1.67465           |
| $c' (a_e)$             | 1.26661                                                                                                     | 1.38295                                              | 1.43087              | 1.43087                     | 1.43087                     | 1.43087              | 1.04566                                                          | 1.05553                                   | 1.05661           |
| Bond Length $2c' (A)$  | 1.34052                                                                                                     | 1.46365                                              | 1.51437              | 1.51437                     | 1.51437                     | 1.51437              | 1.10668                                                          | 1.11713                                   | 1.11827           |
| Exp. Bond Length $(A)$ | 1.349 (1,3-butadiene)<br>1.342 (1,3-cyclopentadiene)<br>1.342 (1,3-cyclopentadiene)<br>1.342 (cyclopentene) | 1.467 (1,3-butadiene)<br>1.469 (1,3-cyclopentadiene) | 1.519 (cyclopentene) | 1.509 (1,3-cyclopentadiene) | 1.509 (1,3-cyclopentadiene) | 1.546 (cyclopentene) | 1.107 (2-methylpropane)<br>1.108 (avg.)<br>1.117 (1,3-butadiene) | 1.107 (C-H propane)<br>1.117 (C-H butane) | 1.122 (isobutane) |
| $h, c (a_e)$           | 0.75055                                                                                                     | 1.32110                                              | 1.46439              | 1.46439                     | 1.46439                     | 1.46439              | 1.26354                                                          | 1.29569                                   | 1.29924           |
| $e$                    | 0.86030                                                                                                     | 0.72309                                              | 0.69887              | 0.69887                     | 0.69887                     | 0.69887              | 0.63756                                                          | 0.63159                                   | 0.63095           |



Table 15.210. The energy parameters (eV) of functional groups of cyclic and conjugated alkenes.

| Parameters                       | C=C<br>Group | C'-C' (a)<br>Group | C'-C' (b)<br>Group | C'-C' (c)<br>Group | C'-C' (d)<br>Group | C'-C' (e)<br>Group | CH <sub>2</sub> (i)<br>Group | CH <sub>3</sub><br>Group | CH <sub>2</sub> (ii)<br>Group | C-H<br>Group |
|----------------------------------|--------------|--------------------|--------------------|--------------------|--------------------|--------------------|------------------------------|--------------------------|-------------------------------|--------------|
| $\eta_1$                         | 2            | 1                  | 1                  | 1                  | 1                  | 1                  | 2                            | 3                        | 2                             | 1            |
| $\eta_2$                         | 0            | 0                  | 0                  | 0                  | 0                  | 0                  | 1                            | 2                        | 1                             | 0            |
| $\eta_3$                         | 0            | 0                  | 0                  | 0                  | 0                  | 0                  | 0                            | 0                        | 0                             | 0            |
| $\zeta_1$                        | 0.5          | 0.5                | 0.5                | 0.5                | 0.5                | 0.5                | 0.75                         | 0.75                     | 0.75                          | 0.75         |
| $\zeta_2$                        | 0.91771      | 1                  | 1                  | 1                  | 1                  | 1                  | 1                            | 1                        | 1                             | 1            |
| $\zeta_3$                        | 1            | 1                  | 1                  | 1                  | 1                  | 1                  | 1                            | 1                        | 1                             | 1            |
| $\zeta_4$                        | 0.91771      | 0.91771            | 0.91771            | 0.91771            | 0.91771            | 0.91771            | 0.91771                      | 0.91771                  | 0.91771                       | 0.91771      |
| $\zeta_5$                        | 0            | 0                  | 0                  | 0                  | 0                  | 0                  | 1                            | 0                        | 1                             | 1            |
| $\zeta_6$                        | 4            | 2                  | 2                  | 2                  | 2                  | 2                  | 1                            | 1                        | 1                             | 1            |
| $\zeta_7$                        | 0            | 0                  | 0                  | 0                  | 0                  | 0                  | 2                            | 3                        | 2                             | 1            |
| $\zeta_8$                        | 0.5          | 0.5                | 0.5                | 0.5                | 0.5                | 0.5                | 0.75                         | 0.75                     | 0.75                          | 0.75         |
| $\zeta_9$                        | 0.91771      | 1                  | 1                  | 1                  | 1                  | 1                  | 1                            | 1                        | 1                             | 1            |
| $\zeta_{10}$                     | -102.08992   | -33.01226          | -30.19634          | -30.19634          | -30.19634          | -28.79214          | -72.03287                    | -107.32728               | -70.41425                     | -35.12015    |
| $V_e$ (eV)                       | 21.48386     | 9.83824            | 9.50874            | 9.50874            | 9.50874            | 9.33352            | 26.02344                     | 38.92728                 | 25.78002                      | 12.87680     |
| $V_p$ (eV)                       | 34.67062     | 8.63041            | 7.37432            | 7.37432            | 7.37432            | 6.77464            | 21.95990                     | 32.53914                 | 21.06675                      | 10.48582     |
| $V_m$ (eV)                       | -17.33551    | -4.31520           | -3.68716           | -3.68716           | -3.68716           | -3.38732           | -10.97995                    | -16.26957                | -10.53337                     | -5.24291     |
| $E_{1,100}$ (eV)                 | 0            | -14.63489          | -14.63489          | -14.63489          | -14.63489          | -15.56407          | -14.63489                    | -15.56407                | -15.56407                     | -14.63489    |
| $\Delta E_{1,100}$ (eV)          | 0            | -1.85836           | 0                  | 0                  | 0                  | 0                  | 0                            | 0                        | 0                             | 0            |
| $E_p$ (eV)                       | 0            | -12.77653          | -14.63489          | -14.63489          | -14.63489          | -15.56407          | -14.63489                    | -15.56407                | -15.56407                     | -14.63489    |
| $E_p$ (eV)                       | -63.27075    | -31.63535          | -31.63534          | -31.63534          | -31.63534          | -31.63537          | -49.66437                    | -67.69451                | -49.66493                     | -31.63533    |
| $E_p$ (eV)                       | -2.26759     | -2.26759           | -1.85836           | -1.85836           | -1.85836           | -1.85836           | 0                            | 0                        | 0                             | 0            |
| $E_p$ (eV)                       | -65.53833    | -33.90295          | -33.49373          | -33.49373          | -33.49373          | -33.49373          | -49.66493                    | -67.69450                | -49.66493                     | -31.63537    |
| $\omega$ (10 <sup>6</sup> rad/s) | 43.0680      | 11.0522            | 9.97851            | 23.3291            | 9.97851            | 9.43699            | 25.2077                      | 24.9286                  | 24.2751                       | 24.1759      |
| $E_k$ (eV)                       | 28.34813     | 7.27475            | 6.56803            | 15.35563           | 6.56803            | 6.21159            | 16.59214                     | 16.40846                 | 15.97831                      | 15.91299     |
| $\bar{E}_D$ (eV)                 | -0.34517     | -0.18090           | -0.16982           | -0.25966           | -0.16982           | -0.16515           | -0.25493                     | -0.25352                 | -0.25017                      | -0.24966     |
| $\bar{E}_{D,100}$ (eV)           | 0.17897      | 0.14829            | 0.11159            | 0.11159            | 0.11159            | 0.12312            | 0.35532                      | 0.35532                  | 0.35532                       | 0.35532      |
| $\bar{E}_{D,100}$ (eV)           | -0.25568     | -0.10676           | -0.11402           | -0.20386           | -0.11402           | -0.10359           | -0.07727                     | -0.22757                 | -0.14502                      | -0.07200     |
| $E_{mag}$ (eV)                   | 0.14803      | 0.14803            | 0.14803            | 0.14803            | 0.14803            | 0.14803            | 0.14803                      | 0.14803                  | 0.14803                       | 0.14803      |
| $E_p$ (eV)                       | -66.04969    | -34.00972          | -33.60776          | -33.60776          | -33.60776          | -33.59732          | -49.81948                    | -67.92207                | -49.80996                     | -31.70737    |
| $E_{mag}$ (eV)                   | -14.63489    | -14.63489          | -14.63489          | -14.63489          | -14.63489          | -14.63489          | -14.63489                    | -14.63489                | -14.63489                     | -14.63489    |
| $E_{mag}$ (eV)                   | 0            | 0                  | 0                  | 0                  | 0                  | 0                  | -13.59844                    | -13.59844                | -13.59844                     | -13.59844    |
| $E_p$ (eV)                       | 7.51014      | 4.73994            | 4.33798            | 4.42782            | 4.18995            | 4.32754            | 7.83968                      | 12.49186                 | 7.83016                       | 3.32601      |

Table 15.211. The total bond energies of cyclic and conjugated alkenes calculated using the functional group composition and the energies of Table 15.210 compared to the experimental values [2]. The magnetic energy  $E_{mag}$  that is subtracted from the 5 weighted sum of the  $E_{p,i(mag)}$  (eV) values based on composition is given by (15.58).

| Formula                       | Name                | C=C | C'-C' (a) | C'-C' (b) | C'-C' (c) | C'-C' (d) | C'-C' (e) | CH | CH <sub>2</sub> (i) | CH <sub>3</sub> | CH <sub>2</sub> (ii) | CH | $E_{mag}$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|-------------------------------|---------------------|-----|-----------|-----------|-----------|-----------|-----------|----|---------------------|-----------------|----------------------|----|-----------|-----------------------------------|-------------------------------------|----------------|
| C <sub>4</sub> H <sub>6</sub> | 1,3 Butadiene       | 2   | 1         | 0         | 0         | 0         | 0         | 2  | 0                   | 0               | 0                    | 2  | 0         | 42.12705                          | 42.12705                            | 0.00084        |
| C <sub>4</sub> H <sub>6</sub> | 1,3 Pentadiene      | 2   | 1         | 1         | 0         | 0         | 0         | 0  | 0                   | 1               | 0                    | 0  | 0         | 54.42484                          | 54.42484                            | 0.00031        |
| C <sub>4</sub> H <sub>6</sub> | 1,4 Pentadiene      | 2   | 0         | 0         | 2         | 0         | 0         | 2  | 0                   | 0               | 1                    | 2  | 0         | 54.03745                          | 54.11866                            | 0.00149        |
| C <sub>5</sub> H <sub>8</sub> | 1,3 Cyclopentadiene | 2   | 1         | 0         | 0         | 2         | 0         | 1  | 1                   | 0               | 1                    | 4  | 0         | 49.27432                          | 49.30294                            | 0.00058        |
| C <sub>5</sub> H <sub>8</sub> | Cyclopentene        | 1   | 0         | 2         | 0         | 0         | 0         | 2  | 3                   | 0               | 2                    | 2  | -1        | 54.83565                          | 54.86117                            | 0.00047        |

Table 15.2.12. The bond angle parameters of cyclic and conjugated alkenes and experimental values [1]. In the calculation of  $\theta_r$ , the parameters from the preceding angle were used.  $E_r$  is  $E_r(atom - atom, msp, AO)$ .

| Atoms of Angle                                                          | $2c_1$<br>Bond 1<br>( $a_0$ ) | $2c_2$<br>Bond 2<br>( $a_0$ ) | $2c_3$<br>Terminal<br>Atom<br>( $a_0$ ) | $E_r$<br>Terminal<br>Atom 1<br>(Table 15.3.A) | Atom 1<br>Hybridization<br>Designation<br>(Table 15.3.A) | $c_2$<br>Atom 1 | $c_2$<br>Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c'_1$  | $E_r$<br>(eV) | $\theta_r$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | Cal. $\theta$<br>( $^\circ$ ) | Exp. $\theta$<br>( $^\circ$ )                                                                                                               |
|-------------------------------------------------------------------------|-------------------------------|-------------------------------|-----------------------------------------|-----------------------------------------------|----------------------------------------------------------|-----------------|-----------------|-------|-------|-------|---------|---------------|----------------------------|----------------------------|----------------------------|-------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------|
| $\angle HC_1H$<br>$H_1C_1 = C_h$<br>1,3-butadiene                       | 2.09132                       | 2.09132                       | 3.4928                                  | -15.95955                                     | 9                                                        | 0.85252         | 1               | 1     | 1     | 0.75  | 1.17300 | 0             |                            |                            |                            | 113.25                        |                                                                                                                                             |
| $\angle C_1C_2H_u$<br>$H_1C_1 = C_h$<br>1,3-butadiene                   |                               |                               |                                         |                                               |                                                          |                 |                 |       |       |       |         |               |                            | 113.25                     |                            | 123.38                        | 120.9<br>(1,3-butadiene)                                                                                                                    |
| $\angle C_1C_2H_u$<br>$H_1C_1 = C_h$<br>1,3-butadiene                   | 2.53321                       | 2.09132                       | 4.0000                                  | -15.95954                                     | 9                                                        | 0.85252         | 0.85252         | 0.75  | 1     | 0.75  | 1.00000 | 0             |                            |                            |                            | 119.45                        | 120.9<br>(1,3-butadiene)                                                                                                                    |
| $\angle C_1C_2C_h$<br>$C_h = C'_h$<br>1,3-butadiene                     | 2.53321                       | 2.76590                       | 4.6904                                  | -16.88873                                     | 27                                                       | 0.80561         | 0.79597         | 1     | 1     | 1     | 0.85395 | -1.85336      |                            |                            |                            | 124.48                        | 124.4<br>(1,3-butadiene CCC)<br>124.4<br>(1,3,5-hexatriene<br>C6CC6)<br>121.7<br>(1,3,5-hexatriene<br>C6C6C6)<br>125.3<br>(2-butene C6C6C6) |
| $\angle C_1C_2C'_h$<br>$C_h = C'_h$<br>1,3-cyclopentadiene              | 2.53321                       | 2.76590                       | 4.3012                                  | -17.81791                                     | 46                                                       | 0.76360         | 0.76360         | 1     | 1     | 1     | 0.76360 | -1.85336      |                            |                            |                            | 108.44                        | 109.4<br>(1,3-cyclopentadiene)                                                                                                              |
| $\angle C_1C_2C'_h$<br>$C_h = C'_h$<br>1,3-cyclopentadiene              | 2.86175                       | 2.53321                       | 4.3818                                  | -17.61330                                     | 42                                                       | 0.77247         | 0.77247         | 1     | 1     | 1     | 0.77247 | -1.85336      |                            |                            |                            | 108.47                        | 109.3<br>(1,3-cyclopentadiene)                                                                                                              |
| $\angle C_1C_2C_h$<br>$= C_h, HC_1H_2(H) =$<br>1,3-cyclopentadiene      | 2.86175                       | 2.86175                       | 4.4609                                  | -17.40869                                     | 38                                                       | 0.78155         | 0.78155         | 1     | 1     | 1     | 0.78155 | -1.85336      |                            |                            |                            | 102.41                        | 102.8<br>(1,3-cyclopentadiene)                                                                                                              |
| $\angle C_1C_2C'_h$<br>$-H_1C_1, HC_1 = C_h, HC_1H_2 -$<br>cyclopentene | 2.86175                       | 2.53321                       | 4.4272                                  | -17.40869                                     | 38                                                       | 0.78155         | 0.77247         | 1     | 1     | 1     | 0.77701 | -1.85336      |                            |                            |                            | 110.14                        | 110.0<br>(cyclopentene)                                                                                                                     |
| $\angle C_1C_2C'_h$<br>$-H_1C_1, HC_1, HC_1 = C_h, H -$<br>cyclopentene | 2.91548                       | 2.86175                       | 4.5166                                  | -17.20408                                     | 35                                                       | 0.79085         | 0.78155         | 1     | 1     | 1     | 0.78620 | -1.85336      |                            |                            |                            | 102.85                        | 103.0<br>(cyclopentene)                                                                                                                     |
| $\angle C_1C_2C_h$<br>$-C_h, HC_1, HC_1H_2 -$<br>cyclopentene           | 2.91548                       | 2.91548                       | 4.5826                                  | -17.20408                                     | 35                                                       | 0.79085         | 0.79085         | 1     | 1     | 1     | 0.79085 | -1.85336      |                            |                            |                            | 103.61                        | 104.0<br>(cyclopentene)                                                                                                                     |

## AROMATIC AND HETEROCYCLIC COMPOUNDS

Aromatic and heterocyclic molecules comprise at least one of an aromatic or a cyclic conjugated alkene functional group. The latter was described in the Cyclic and Conjugated Alkenes section. The aromatic bond is uniquely stable and requires the sharing of the electrons of multiple  $H_2$ -type MOs. The results of the derivation of the parameters of the benzene molecule given in the Benzene Molecule ( $C_6H_6$ ) section can be generalized to any aromatic function group(s) of aromatic and heterocyclic compounds.

$C_6H_6$  can be considered a linear combination of three ethylene molecules wherein a  $C-H$  bond of each  $CH_2$  group of  $H_2C=CH_2$  is replaced by a  $C=C$  bond to form a six-member ring of carbon atoms. The solution of the ethylene molecule is given in the Ethylene Molecule ( $CH_2CH_2$ ) section. The radius  $r_{ethylene, 2sp^3}$  ( $0.85252a_0$ ) of the  $C2sp^3$  shell of ethylene calculated from the Coulombic energy is given by Eq. (14.244). The Coulombic energy  $E_{Coulomb}(C_{ethylene}, 2sp^3)$  ( $-15.95955 eV$ ) of the outer electron of the  $C2sp^3$  shell is given by Eq. (14.245). The energy  $E(C_{ethylene}, 2sp^3)$  ( $-15.76868 eV$ ) of the outer electron of the  $C2sp^3$  shell is given by Eq. (14.246).  $E_T(C=C, 2sp^3)$  ( $-1.13380 eV$ ) (Eq. (14.247), the energy change of each  $C2sp^3$  shell with the formation of the  $C=C$ -bond MO is given by the difference between  $E(C_{ethylene}, 2sp^3)$  and  $E(C, 2sp^3)$ .  $C_6H_6$  can be solved using the same principles as those used to solve ethylene wherein the  $2s$  and  $2p$  shells of each  $C$  hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Each  $2sp^3$  HO of each carbon atom initially has four unpaired electrons. Thus, the 6  $H$  atomic orbitals (AOs) of benzene contribute six electrons and the six  $sp^3$ -hybridized carbon atoms contribute twenty-four electrons to form six  $C-H$  bonds and six  $C=C$  bonds. Each  $C-H$  bond has two paired electrons with one donated from the  $H$  AO and the other from the  $C2sp^3$  HO. Each  $C=C$  bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from two sets of two  $C2sp^3$  HOs of the participating carbon atoms. Each  $C-H$  and each  $C=C$  bond comprises a linear combination

of one and two diatomic  $H_2$ -type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section, respectively.

Consider the case where three sets of  $C = C$ -bond MOs form bonds between the two carbon atoms of each molecule to form a six-member ring such that the six resulting bonds  
5 comprise eighteen paired electrons. Each bond comprises a linear combination of two MOs wherein each comprises two  $C2sp^3$  HOs and 75% of a  $H_2$ -type ellipsoidal MO divided between the  $C2sp^3$  HOs:

$$\left( \begin{array}{l} 3(2 C2sp^3 + 0.75 H_2 MO) \rightarrow 3(C=C)^{4e} - \text{ethylene-type-bond MO} \\ \rightarrow 6(C=C)^{3e} - \text{bond MO of benzene} \end{array} \right) \quad (15.142)$$

10 The linear combination of each  $H_2$ -type ellipsoidal MO with each  $C2sp^3$  HO further comprises an excess 25% charge-density contribution per bond from each  $C2sp^3$  HO to the  $C = C$ -bond MO to achieve an energy minimum. Thus, the dimensional parameters of each bond  $C = C$ -bond are determined using Eqs. (15.42) and (15.1-15.5) in a form that are the same equations as those used to determine the same parameters of the  $C = C$ -bond MO of ethylene (Eqs. (14.242-  
15 14.268)) while matching the boundary conditions of the structure of benzene.

Hybridization with 25% electron donation to each  $C = C$ -bond gives rise to the  $C_{benzene} 2sp^3$  HO-shell Coulombic energy  $E_{Coulomb}(C_{benzene}, 2sp^3)$  given by Eq. (14.245). To meet the equipotential condition of the union of the six  $C2sp^3$  HOs,  $c_2$  and  $C_2$  of Eq. (15.42) for the aromatic  $C=C^{3e}$ -bond MO is given by Eq. (15.62) as the ratio of 15.95955 eV, the magnitude of  
20  $E_{Coulomb}(C_{benzene}, 2sp^3)$  (Eq. (14.245)), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of  $H$  (Eq. (1.243)):

$$C_2(benzene C2sp^3 HO) = c_2(benzene C2sp^3 HO) = \frac{13.605804 \text{ eV}}{15.95955 \text{ eV}} = 0.85252 \quad (15.143)$$

The energies of each  $C=C^{3e}$  bond of benzene are also determined using the same equations as those of ethylene (Eqs. (14.251-14.253) and (14.319-14.333) with the parameters of  
25 benzene. Ethylene serves as a basis element for the  $C=C^{3e}$  bonding of benzene wherein each of the six  $C=C^{3e}$  bonds of benzene comprises  $(0.75)(4) = 3$  electrons according to Eq. (15.142).

The total energy of the bonds of the eighteen electrons of the  $C \equiv C^{3e}$  bonds of benzene,  $E_T(C_6H_6, C \equiv C^{3e})$ , is given by (6)(0.75) times  $E_{T+osc}(C = C)$  (Eq. (14.492)), the total energy of the  $C \equiv C^{3e}$ -bond MO of benzene including the Doppler term, minus eighteen times  $E(C, 2sp^3)$  (Eq. (14.146)), the initial energy of each  $C2sp^3$  HO of each  $C$  that forms the  $C \equiv C^{3e}$  bonds of bond order two. Thus, the total energy of the six  $C \equiv C^{3e}$  bonds of benzene with three electron per aromatic bond given by Eq. (14.493) is

$$\begin{aligned} E_T(C_6H_6, C \equiv C^{3e}) &= (6)(0.75)E_{T+osc}(C = C) - (6)(3)E(C, 2sp^3) \\ &= (6)(0.75)(-66.05796 \text{ eV}) - 18(-14.63489 \text{ eV}) \\ &= -297.26081 \text{ eV} - (-263.42798 \text{ eV}) \\ &= -33.83284 \text{ eV} \end{aligned} \quad (15.144)$$

The results of benzene can be generalized to the class of aromatic and heterocyclic compounds.

$E_{hv}$  of an aromatic bond is given by  $E_T(H_2)$  (Eqs. (11.212) and (14.486)), the maximum total energy of each  $H_2$ -type MO such that

$$\bar{E}_{osc} = n_1(\bar{E}_D + \bar{E}_{Kvib}) = n_1 \left( -31.63536831 \text{ eV} \sqrt{\frac{2\bar{E}_K}{Mc^2}} + \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} \right) \quad (15.145)$$

The factor of 0.75 corresponding to the three electrons per aromatic bond of bond order two given in the Benzene Molecule ( $C_6H_6$ ) section modifies Eqs. (15.52-15.56). Multiplication of the total energy given by Eq. (15.55) by  $f_1 = 0.75$  with the substitution of Eq. (15.145) gives the

total energy of the aromatic bond:

$$E_T(\text{Group}) = f_1 \left( \begin{aligned} &E(\text{basis energies}) + E_T(\text{atom-atom, } msp^3 \text{ AO}) \\ &-31.63536831 \text{ eV} \sqrt{\frac{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^2}{4\pi\epsilon_o R^3}}}{m_e c^2} + n_1\bar{E}_{Kvib} + c_3\frac{8\pi\mu_o\mu_B^2}{r^3}} \end{aligned} \right) \quad (15.146)$$



The total bond energy of the aromatic group  $E_D(\text{Group})$  is the negative difference of the total energy of the group (Eq. (15.146)) and the total energy of the starting species given by the sum of  $c_4 E_{\text{initial}}(c_4 \text{ AO} / \text{HO})$  and  $c_5 E_{\text{initial}}(c_5 \text{ AO} / \text{HO})$ :

$$E_D(\text{Group}) = - \left[ f_1 \left( \begin{aligned} & E(\text{basis energies}) + E_T(\text{atom} - \text{atom}, \text{msp}^3 \text{ AO}) \\ & - 31.63536831 \text{ eV} \sqrt{\frac{2\hbar \sqrt{\frac{C_{1o} C_{2o} e^2}{4\pi\epsilon_o R^3}}}{m_e}} + n_1 \bar{E}_{\text{Kvib}} + c_3 \frac{8\pi\mu_o \mu_B^2}{r^3} \end{aligned} \right) - (c_4 E_{\text{initial}}(\text{AO} / \text{HO}) + c_5 E_{\text{initial}}(c_5 \text{ AO} / \text{HO})) \right] \quad (15.147)$$

5 Since there are three electrons per aromatic bond,  $c_4$  is three times the number of aromatic bonds.

Benzene can also be considered as comprising chemical bonds between six  $\text{CH}$  radicals wherein each radical comprises a chemical bond between carbon and hydrogen atoms. The solution of the parameters of  $\text{CH}$  is given in the Hydrogen Carbide ( $\text{CH}$ ) section. Those of the  
10 benzene are given in the Benzene Molecule ( $\text{C}_6\text{H}_6$ ) section. The energy components of  $V_e$ ,  $V_p$ ,  $T$ ,  $V_m$ , and  $E_T$  are the same as those of the hydrogen carbide radical, except that  $E_T(C = C, 2sp^3) = -1.13379 \text{ eV}$  (Eq. (14.247)) is subtracted from  $E_T(\text{CH})$  of Eq. (13.495) to match the energy of each  $\text{C}-\text{H}$ -bond MO to the decrease in the energy of the corresponding  $\text{C}2sp^3$  HO. In the corresponding generalization of the aromatic  $\text{CH}$  group, the geometrical  
15 parameters are determined using Eq. (15.42) and Eqs. (15.1-15.5) with  $E_T(\text{atom} - \text{atom}, \text{msp}^3 \text{ AO}) = -1.13379 \text{ eV}$ .

The total energy of the benzene  $\text{C}-\text{H}$ -bond MO,  $E_{T_{\text{benzene}}}(C-H)$ , given by Eq. (14.467) is the sum of  $0.5E_T(C = C, 2sp^3)$ , the energy change of each  $\text{C}2sp^3$  shell per single bond due to the decrease in radius with the formation of the corresponding  $\text{C}=\text{C}$ -bond MO (Eq. (14.247)),  
20 and  $E_{T_{\text{benzene}}}(\text{CH})$ , the  $\sigma$  MO contribution given by Eq. (14.441). In the corresponding generalization of the aromatic  $\text{CH}$  group, the energy parameters are determined using Eqs. (15.146-15.147) with  $f_1 = 1$  and  $E_T(\text{atom} - \text{atom}, \text{msp}^3 \text{ AO}) = \frac{-1.13379 \text{ eV}}{2}$ . Thus, the energy

contribution to the single aromatic  $CH$  bond is one half that of the  $C=C$  double bond contribution. This matches the energies of the  $CH$  and  $C=C$  aromatic groups, conserves the electron number with the equivalent charge density as that of  $s=1$  in Eqs. (15.18-15.21), and further gives a minimum energy for the molecule. Breakage of the aromatic  $C=C$  bonds to give  $CH$  groups creates unpaired electrons in these fragments that corresponds to  $c_3=1$  in Eq. (15.56) with  $E_{mag}$  given by Eq. (15.58).

Each of the  $C-H$  bonds of benzene comprises two electrons according to Eq. (14.439). From the energy of each  $C-H$  bond,  $-E_{D_{benzene}}(^{12}CH)$  (Eq. (14.477)), the total energy of the twelve electrons of the six  $C-H$  bonds of benzene,  $E_T(C_6H_6, C-H)$ , given by Eq. (14.494) is

$$E_T(C_6H_6, C-H) = (6) \left( -E_{D_{benzene}}(^{12}CH) \right) = 6(-3.90454 \text{ eV}) = -23.42724 \text{ eV} \quad (15.148)$$

The total bond dissociation energy of benzene,  $E_D(C_6H_6)$ , given by Eq. (14.495) is the negative sum of  $E_T(C_6H_6, C=C)$  (Eq. (14.493)) and  $E_T(C_6H_6, C-H)$  (Eq. (14.494)):

$$\begin{aligned} E_D(C_6H_6) &= - \left( E_T(C_6H_6, C=C) + E_T(C_6H_6, C-H) \right) \\ &= - \left( (-33.83284 \text{ eV}) + (-23.42724 \text{ eV}) \right) \\ &= 57.2601 \text{ eV} \end{aligned} \quad (15.149)$$

Using the parameters given in Tables 15.214 and 15.216 in the general equations (Eqs. (15.42), (15.1-15.5), and (15.146-15.147)) reproduces the results for benzene given in the Benzene Molecule ( $C_6H_6$ ) section as shown in Tables 15.214 and 15.216.

The symbols of the functional groups of aromatics and hertocyclics are given in Table 15.213. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aromatics and hertocyclics are given in Tables 15.214, 15.215, and 15.216, respectively. The total energy of benzene given in Table 15.217 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.216 corresponding to functional-group composition of the molecule. The bond angle parameters of benzene determined using Eqs. (15.79-15.108) are given in Table 15.218.

Table 15.213. The symbols of functional groups of aromatics and heterocyclics.

| Functional Group   | Group Symbol           |
|--------------------|------------------------|
| CC (aromatic bond) | $\text{C}^{\text{ar}}$ |
| CH (aromatic)      | $\text{CH}(\text{I})$  |

Table 15.214. The geometrical bond parameters of aromatics and heterocyclics and experimental values [1].

| Parameter                          | $\text{C}^{\text{ar}}$ Group | CH Group        |
|------------------------------------|------------------------------|-----------------|
| $a$ ( $a_0$ )                      | 1.47348                      | 1.60061         |
| $c'$ ( $a_0$ )                     | 1.31468                      | 1.03299         |
| Bond Length $2c'$ ( $\text{\AA}$ ) | 1.39140                      | 1.09327         |
| Exp. Bond Length ( $\text{\AA}$ )  | 1.399 (benzene)              | 1.101 (benzene) |
| $h, c$ ( $a_0$ )                   | 0.66540                      | 1.22265         |
| $e$                                | 0.89223                      | 0.64537         |

5 Table 15.215. The MO to HO intercept geometrical bond parameters of benzene.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{exp}^2, \text{AO})$ .

| Bond                                                               | Atom           | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $\text{C}^{\text{ar}}$ (eV) | $r_{\text{final}}$ ( $a_0$ ) | $E_{\text{total}}(\text{C}^{\text{ar}})$ (eV) Final | $\bar{E}(\text{C}^{\text{ar}})$ (eV) Final | $\theta'$ ( $^\circ$ ) | $\theta_1$ ( $^\circ$ ) | $\theta_2$ ( $^\circ$ ) | $d_1$ ( $a_0$ ) | $d_2$ ( $a_0$ ) |
|--------------------------------------------------------------------|----------------|-------------------|-------------------|-------------------|-------------------|------------------------------------------------|------------------------------|-----------------------------------------------------|--------------------------------------------|------------------------|-------------------------|-------------------------|-----------------|-----------------|
| $\text{C}^{\text{ar}} - \text{H}(\text{CH})$                       | C              | -0.85035          | -0.85035          | -0.85035          | 0                 | -153.88327                                     | 0.91771                      | -17.09334                                           | -16.90248                                  | 74.42                  | 105.58                  | 38.84                   | 1.24678         | 0.21379         |
| $\text{C}^{\text{ar}} = \text{H}(\text{C}^{\text{ar}} = \text{C})$ | C <sub>u</sub> | -0.85035          | -0.85035          | -0.56690          | 0                 | -153.88327                                     | 0.91771                      | -17.09334                                           | -16.90248                                  | 134.24                 | 45.76                   | 58.98                   | 0.75935         | 0.55533         |

Table 15.216. The energy parameters (eV) of functional groups of aromatics and hertocyclics.

| Parameters                        | <sup>3s</sup><br>C=C<br>Group | CH<br>Group             |
|-----------------------------------|-------------------------------|-------------------------|
| $f_1$                             | 0.75                          | 1                       |
| $n_1$                             | 2                             | 1                       |
| $n_2$                             | 0                             | 0                       |
| $n_3$                             | 0                             | 0                       |
| $C_1$                             | 0.5                           | 0.75                    |
| $C_2$                             | 0.85252                       | 1                       |
| $c_1$                             | 1                             | 1                       |
| $c_2$                             | 0.85252                       | 0.91771                 |
| $c_3$                             | 0                             | 1                       |
| $c_4$                             | 3                             | 1                       |
| $c_5$                             | 0                             | 1                       |
| $C_{1o}$                          | 0.5                           | 0.75                    |
| $C_{2o}$                          | 0.85252                       | 1                       |
| $V_u$ (eV)                        | -101.12679                    | -37.10024               |
| $V_p$ (eV)                        | 20.69825                      | 13.17125                |
| $T$ (eV)                          | 34.31559                      | 11.58941                |
| $V_m$ (eV)                        | -17.15779                     | -5.79470                |
| $E_{(AOIHO)}$ (eV)                | 0                             | -14.63489               |
| $\Delta E_{H_2MO(AOIHO)}$ (eV)    | 0                             | -1.13379                |
| $E_T(AOIHO)$ (eV)                 | 0                             | -13.50110               |
| $E_T(H_2MO)$ (eV)                 | -63.27075                     | -31.63539               |
| $E_T(atom - atom, msp^3.AO)$ (eV) | -2.26759                      | -0.56690                |
| $E_T(MO)$ (eV)                    | -65.53833                     | -32.20226               |
| $\omega$ ( $10^{15}$ rad / s)     | 49.7272                       | 26.4826                 |
| $E_K$ (eV)                        | 32.73133                      | 17.43132                |
| $\bar{E}_D$ (eV)                  | -0.35806                      | -0.26130                |
| $\bar{E}_{Kvib}$ (eV)             | 0.19649<br>[49]               | 0.35532<br>Eq. (13.458) |
| $\bar{E}_{osc}$ (eV)              | -0.25982                      | -0.08364                |
| $E_{mag}$ (eV)                    | 0.14803                       | 0.14803                 |
| $E_T(Group)$ (eV)                 | -49.54347                     | -32.28590               |
| $E_{initial}(c_4 AOIHO)$ (eV)     | -14.63489                     | -14.63489               |
| $E_{initial}(c_5 AOIHO)$ (eV)     | 0                             | -13.59844               |
| $E_D(Group)$ (eV)                 | 5.63881                       | 3.90454                 |

Table 15.217. The total bond energies of benzene calculated using the functional group composition and the energies of Table 15.216 compared to the experimental values [2].

| Formula  | Name    | $\sum C=C$ | $\sum C-H$ | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond Energy<br>(eV) | Relative<br>Error |
|----------|---------|------------|------------|-----------------------------------------|-------------------------------------------|-------------------|
| $C_6H_6$ | Benzene | 6          | 6          | 57.26008                                | 57.26340                                  | 0.00006           |

Table 15.218. The bond angle parameters of benzene and experimental values [1].  $E_T$  is  $E_T(atom - atom, msp, AO)$ .

| Atoms of Angle              | $2c_1'$<br>Bond 1<br>( $\sigma_g$ ) | $2c_2'$<br>Bond 2<br>( $\sigma_g$ ) | $2c_3'$<br>Terminal<br>Atoms<br>( $\sigma_g$ ) | $E_{\text{terminal-atom 1}}$<br>Atom 1 | Atom 1<br>Hybridization<br>Designation<br>(Table 15.3.A) | $E_{\text{terminal-atom 2}}$<br>Atom 2 | Atom 2<br>Hybridization<br>Designation<br>(Table 15.3.A) | $c_2$<br>Atom 1 | $c_2$<br>Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$  | $E_T$<br>(eV) | $\theta_r$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | Cal. $\theta$<br>( $^\circ$ ) | Exp. $\theta$<br>( $^\circ$ ) |
|-----------------------------|-------------------------------------|-------------------------------------|------------------------------------------------|----------------------------------------|----------------------------------------------------------|----------------------------------------|----------------------------------------------------------|-----------------|-----------------|-------|-------|-------|---------|---------------|----------------------------|----------------------------|----------------------------|-------------------------------|-------------------------------|
| $\angle(C-C)$<br>(aromatic) | 2.62936                             | 2.62936                             | 4.5585                                         | -17.17218                              | 34                                                       | -17.17218                              | 34                                                       | 0.79232         | 0.79232         | 1     | 1     | 1     | 0.79232 | -1.55536      |                            |                            |                            | 120.19                        | 120 [50-52]<br>(benzene)      |
| $\angle(C-H)$<br>(aromatic) |                                     |                                     |                                                |                                        |                                                          |                                        |                                                          |                 |                 |       |       |       |         |               | 120.19                     |                            |                            | 119.91                        | 120 [50-52]<br>(benzene)      |

## NAPHTHALENE

Naphthalene has the formula  $C_{10}H_8$  and comprises a planar molecule with two aromatic rings that share a common  $C-C$  group. In order to be aromatic, the total number of bonding electrons must be a multiple of 3 since the number of electrons of the aromatic bond is  
 5  $(0.75)(4) = 3$  as shown in the Benzene section. In the case of naphthalene, the peripheral 10 carbons form the aromatic MO with the center bridged by a  $C-C$  single bond. Then, 30 electrons of the 48 available form aromatic bonds, two electrons form the bridging  $C-C$  single bond, and 16 electrons form the eight  $C-H$  single bonds. The energies of the aromatic carbons are given by the same equations as those of benzene (Eqs. (15.42), (15.1-15.5), and  
 10 (15.146-15.147)), except that there are 10 in naphthalene versus six in benzene. Since there are three electrons per aromatic bond,  $c_4$  is three times ten, the number of aromatic bonds. Similarly, the aromatic  $C-H$  group of naphthalene is equivalent to that of benzene.

To meet the equipotential condition of the union of the ten  $C2sp^3$  HOs bridged by the  $C-C$  single bond, the parameters  $c_1$ ,  $C_2$ , and  $C_{2o}$  of Eq. (15.42) are one for the  $C-C$  group,  
 15  $C_{1o}$  and  $C_1$  are 0.5, and  $c_2$  given by Eq. (15.142) is  $c_2(C2sp^3HO) = 0.85252$ . Otherwise, the solutions of the  $C-C$  bond parameters are equivalent to those of the replaced  $C-H$  groups with  $E(AO/HO) = -14.63489 \text{ eV}$  and  $\Delta E_{H_2MO}(AO/HO) = -1.13379 \text{ eV}$  in Eq. (15.41). Similarly, the energy parameters are determined using Eqs. (15.52-15.56) with  

$$E_T(atom - atom, msp^3.AO) = \frac{-1.13379 \text{ eV}}{2}.$$

20 The symbols of the functional groups of naphthalene are given in Table 15.219. The corresponding designation of the structure is shown in Figure 62. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of naphthalene are given in Tables 15.220, 15.221, and 15.222, respectively. The total energy of naphthalene given in Table 15.223 was calculated as the sum  
 25 over the integer multiple of each  $E_D(\text{Group})$  of Table 15.222 corresponding to functional-group composition of the molecule. The bond angle parameters of naphthalene determined using Eqs. (15.79-15.108) are given in Table 15.224.

Table 15.219. The symbols of functional groups of naphthalene.

| Functional Group                                 | Group Symbol |
|--------------------------------------------------|--------------|
| C=C (aromatic bond)                              | C=C          |
| CH (aromatic)                                    | CH (i)       |
| C <sub>sp</sub> -C <sub>sp</sub> (bridging bond) | C-C          |

Table 15.220. The geometrical bond parameters of naphthalene and experimental values [1].

| Parameter                | C=C Group                    | CH Group           | C-C Group             |
|--------------------------|------------------------------|--------------------|-----------------------|
| $\sigma$ (Å)             | 1.47348                      | 1.60661            | 1.75607               |
| $\sigma'$ (Å)            | 1.31468                      | 1.03299            | 1.32517               |
| Bond Length<br>$2c'$ (Å) | 1.39140                      | 1.09327            | 1.40250               |
| Exp. Bond Length<br>(Å)  | 1.40 (avg.)<br>(naphthalene) | 1.101<br>(benzene) | 1.42<br>(naphthalene) |
| $h_{\sigma}c'$ (Å)       | 0.66540                      | 1.22265            | 1.15226               |
| $\sigma$                 | 0.89223                      | 0.64537            | 0.75462               |

Table 15.221. The MO to H0 intercept geometrical bond parameters of naphthalene.  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{msp}, \text{AO})$ .

| Bond                                                                                             | Atom            | $E_r$<br>(eV)<br>Bond 1 | $E_r$<br>(eV)<br>Bond 2 | $E_r$<br>(eV)<br>Bond 3 | $E_r$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>C2sp <sup>3</sup><br>(eV) | $r_{\text{final}}$<br>(Å) | $E_{\text{total}}$ (C2sp <sup>3</sup> )<br>(eV)<br>Final | $E$ (C2sp <sup>3</sup> )<br>(eV)<br>Final | $\theta$<br>(°) | $\theta_1$<br>(°) | $\theta_2$<br>(°) | $d_1$<br>(Å) | $d_2$<br>(Å) |
|--------------------------------------------------------------------------------------------------|-----------------|-------------------------|-------------------------|-------------------------|-------------------------|----------------------------------------------------|---------------------------|----------------------------------------------------------|-------------------------------------------|-----------------|-------------------|-------------------|--------------|--------------|
| C-H (CH)                                                                                         | C               | -0.85035                | -0.85035                | -0.56690                | 0                       | -153.88327                                         | 0.91771                   | -17.09334                                                | -16.90248                                 | 74.42           | 105.58            | 38.84             | 1.24678      | 0.21379      |
| C=HC=C                                                                                           | C <sub>sp</sub> | -0.85035                | -0.85035                | -0.56690                | 0                       | -153.88327                                         | 0.91771                   | -17.09334                                                | -16.90248                                 | 134.24          | 45.76             | 58.98             | 0.75935      | 0.55533      |
| C=C <sub>sp</sub> (C <sub>sp</sub> )=C                                                           | C <sub>sp</sub> | -0.85035                | -0.85035                | -0.38345                | 0                       | -153.59983                                         | 0.91771                   | -16.80989                                                | -16.61903                                 | 134.81          | 45.19             | 59.66             | 0.74439      | 0.57038      |
| (C <sub>sp</sub> ) <sub>2</sub> C <sub>sp</sub> -C <sub>sp</sub> (C <sub>sp</sub> ) <sub>2</sub> | C <sub>sp</sub> | -0.85035                | -0.85035                | -0.38345                | 0                       | -153.59983                                         | 0.91771                   | -16.80989                                                | -16.61903                                 | 99.50           | 80.50             | 47.66             | 1.18269      | 0.14248      |

Table 15.222. The energy parameters (eV) of functional groups of naphthalene.

| Parameters                        | $\overset{3e}{C=C}$<br>Group | CH<br>Group             | C - C<br>Group |
|-----------------------------------|------------------------------|-------------------------|----------------|
| $f_1$                             | 0.75                         | 1                       | 1              |
| $n_1$                             | 2                            | 1                       | 1              |
| $n_2$                             | 0                            | 0                       | 0              |
| $n_3$                             | 0                            | 0                       | 0              |
| $C_1$                             | 0.5                          | 0.75                    | 0.5            |
| $C_2$                             | 0.85252                      | 1                       | 1              |
| $c_1$                             | 1                            | 1                       | 1              |
| $c_2$                             | 0.85252                      | 0.91771                 | 0.85252        |
| $c_3$                             | 0                            | 1                       | 0              |
| $c_4$                             | 3                            | 1                       | 2              |
| $c_5$                             | 0                            | 1                       | 0              |
| $C_{1o}$                          | 0.5                          | 0.75                    | 0.5            |
| $C_{2o}$                          | 0.85252                      | 1                       | 1              |
| $V_e$ (eV)                        | -101.12679                   | -37.10024               | -34.43791      |
| $V_p$ (eV)                        | 20.69825                     | 13.17125                | 10.26723       |
| $T$ (eV)                          | 34.31559                     | 11.58941                | 9.80539        |
| $V_m$ (eV)                        | -17.15779                    | -5.79470                | -4.90270       |
| $E_{AOIHO}$ (eV)                  | 0                            | -14.63489               | -14.63489      |
| $\Delta E_{H_2MO(AOIHO)}$ (eV)    | 0                            | -1.13379                | -1.13379       |
| $E_T(AOIHO)$ (eV)                 | 0                            | -13.50110               | -13.50110      |
| $E_T(H_2MO)$ (eV)                 | -63.27075                    | -31.63539               | -31.63529      |
| $E_T(atom - atom, msp^3.AO)$ (eV) | -2.26759                     | -0.56690                | -0.56690       |
| $E_T(MO)$ (eV)                    | -65.53833                    | -32.20226               | -32.20226      |
| $\omega$ ( $10^{15}$ rad / s)     | 49.7272                      | 26.4826                 | 23.6343        |
| $E_K$ (eV)                        | 32.73133                     | 17.43132                | 15.55648       |
| $\bar{E}_D$ (eV)                  | -0.35806                     | -0.26130                | -0.25127       |
| $\bar{E}_{Kvib}$ (eV)             | 0.19649<br>[49]              | 0.35532<br>Eq. (13.458) | 0.12312<br>[2] |
| $\bar{E}_{osc}$ (eV)              | -0.25982                     | -0.08364                | -0.18971       |
| $E_{mag}$ (eV)                    | 0.14803                      | 0.14803                 | 0.14803        |
| $E_T(Group)$ (eV)                 | -49.54347                    | -32.28590               | -32.39198      |
| $E_{initial}(c_1 AOIHO)$ (eV)     | -14.63489                    | -14.63489               | -14.63489      |
| $E_{initial}(c_3 AOIHO)$ (eV)     | 0                            | -13.59844               | 0              |
| $E_D(Group)$ (eV)                 | 5.63881                      | 3.90454                 | 3.12220        |



Table 15.223. The total bond energies of naphthalene calculated using the functional group composition and the energies of Table 15.222 compared to the experimental values [2].

| Formula                        | Name        | C=C | C <sup>≡</sup> C | C <sup>≡</sup> H | C-C | Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|--------------------------------|-------------|-----|------------------|------------------|-----|-------|-----------------------------------|-------------------------------------|----------------|
| C <sub>10</sub> H <sub>8</sub> | Naphthalene | 10  | 8                | 1                | 1   |       | 90.74658                          | 90.79143                            | 0.00049        |

Table 15.224. The bond angle parameters of naphthalene and experimental values [1].  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{msp}, \text{AO})$ .

| Atoms of Angle                                                 | 2C <sup>1</sup><br>Bond 1<br>(a <sub>1</sub> ) | 2C <sup>2</sup><br>Bond 2<br>(a <sub>2</sub> ) | 2C <sup>3</sup><br>Terminal<br>Atom<br>(a <sub>3</sub> ) | $E_{\text{calc}}^{\text{orbital}}$<br>Atom 1 | Atom 1<br>Hybridization<br>Designation<br>(Table 15.3.A) | $E_{\text{calc}}^{\text{orbital}}$<br>Atom 2 | Atom 2<br>Hybridization<br>Designation<br>(Table 15.3.A) | C <sub>2</sub><br>Atom 1 | C <sub>2</sub><br>Atom 2 | C <sub>1</sub> | C <sub>2</sub> | C <sub>3</sub> | θ <sub>1</sub><br>(°) | θ <sub>2</sub><br>(°) | Cal. θ<br>(°) | Exp. θ<br>(°)            |
|----------------------------------------------------------------|------------------------------------------------|------------------------------------------------|----------------------------------------------------------|----------------------------------------------|----------------------------------------------------------|----------------------------------------------|----------------------------------------------------------|--------------------------|--------------------------|----------------|----------------|----------------|-----------------------|-----------------------|---------------|--------------------------|
| ∠C <sub>1</sub> C <sub>2</sub> C <sub>3</sub><br>(naphthalene) | 2.62936                                        | 2.65034                                        | 4.5585                                                   | -17.17218                                    | 34                                                       | -17.17218                                    | 34                                                       | 0.79232                  | 0.79232                  | 1              | 1              | 1              |                       |                       | 119.40        | 119.4<br>(naphthalene)   |
| ∠C <sub>2</sub> C <sub>3</sub> H<br>(naphthalene)              |                                                |                                                |                                                          |                                              |                                                          |                                              |                                                          |                          |                          |                |                |                | 119.40                |                       | 120.30        |                          |
| ∠CCC<br>(aromatic)                                             | 2.62936                                        | 2.62936                                        | 4.5585                                                   | -17.17218                                    | 34                                                       | -17.17218                                    | 34                                                       | 0.79232                  | 0.79232                  | 1              | 1              | 1              |                       |                       | 120.19        | 120 [50-52]<br>(benzene) |
| ∠CCH<br>(aromatic)                                             |                                                |                                                |                                                          |                                              |                                                          |                                              |                                                          |                          |                          |                |                |                | 120.19                |                       | 119.91        | 120 [50-52]<br>(benzene) |

## TOLUENE

Toluene has the formula  $C_7H_8$  and comprises the benzene molecule with one hydrogen atom replaced by a methyl group corresponding to a  $CH_3$  functional group and a  $C-C$  functional group. The aromatic  $C=C$  and  $C-H$  functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The  $CH_3$  functional group is the same as that of continuous and branched-chain alkanes given in the corresponding sections.

The bond between the methyl and aromatic ring comprises a  $C-C$  functional group that is are solved using the same principles as those used to solve the alkane functional groups wherein the  $2s$  and  $2p$  AOs of each  $C$  hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. To match energies within the MO that bridges methyl and aromatic carbons,  $E(AO/HO)$  and  $\Delta E_{H_2MO}(AO/HO)$  in Eq. (15.41) are  $-15.35946 \text{ eV}$  (Eq. (14.155)) and  $\frac{-1.13379 \text{ eV}}{2}$ , respectively.

To meet the equipotential condition of the union of the aromatic and methyl  $C2sp^3$  HOs of the  $C-C$  single bond, the parameters  $c_1$ ,  $C_2$ , and  $C_{2o}$  of Eq. (15.42) are one for the  $C-C$  group,  $C_{1o}$  and  $C_1$  are 0.5, and  $c_2$  given by Eq. (13.430) is  $c_2(C2sp^3HO) = 0.91771$ . To match the energies of the functional groups,  $E_T(atom - atom, msp^3.AO)$  of the  $C-C$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  atoms to the MO is  $-1.13379 \text{ eV}$  which is the same energy per  $C2sp^3$  HO as that of the replaced  $C-H$  group.

The symbols of the functional groups of toluene are given in Table 15.225. The corresponding designation of the structure is shown in Figure 63. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of toluene are given in Tables 15.226, 15.227, and 15.228, respectively. The total energy of toluene given in Table 15.229 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.228 corresponding to functional-group composition of the molecule. The bond angle parameters of toluene determined using Eqs. (15.79-15.108) are given in Table 15.230.

Table 15.225. The symbols of functional groups of toluene.

| Functional Group                                        | Group Symbol                             |
|---------------------------------------------------------|------------------------------------------|
| CC (aromatic bond)                                      | $\overset{\text{ar}}{\text{C}}-\text{C}$ |
| CH (aromatic)                                           | $\text{C}(\text{H})$                     |
| $\text{C}'-\text{C}'$ ( $\text{CH}_3$ to aromatic bond) | $\text{C}'-\text{C}'$                    |
| $\text{CH}_3$ group                                     | $\text{C}-\text{H}(\text{CH}_3)$         |

Table 15.226. The geometrical bond parameters of toluene and experimental values [1].

| Parameter              | $\overset{\text{ar}}{\text{C}}=\text{C}$ Group | CH (i) Group          | $\text{C}'-\text{C}'$ Group | $\text{C}-\text{H}(\text{CH}_3)$ Group |
|------------------------|------------------------------------------------|-----------------------|-----------------------------|----------------------------------------|
| $a$ ( $a_0$ )          | 1.47348                                        | 1.60061               | 2.06004                     | 1.64920                                |
| $c'$ ( $a_0$ )         | 1.31468                                        | 1.03299               | 1.43528                     | 1.04856                                |
| Bond Length            |                                                |                       |                             |                                        |
| $2c'$ ( $\text{\AA}$ ) | 1.39140                                        | 1.09327               | 1.51904                     | 1.10974                                |
| Exp. Bond Length       | 1.399 (toluene)                                | 1.11 (avg.) (toluene) | 1.524 (toluene)             | 1.11 (avg.) (toluene)                  |
| $h_2c'$ ( $a_0$ )      | 0.66340                                        | 1.22265               | 1.47774                     | 1.27295                                |
| $e$                    | 0.89223                                        | 0.64537               | 0.69673                     | 0.63580                                |

Table 15.227. The MO to HO intercept geometrical bond parameters of toluene.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{resp. AO})$ .

| Bond                                                       | Atom         | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy C2sp <sup>3</sup> (eV) | $r_{\text{final}}$ ( $a_0$ ) | $E_{\text{total}}(\text{C2sp}^3)$ (eV) Final | $E(\text{C2sp}^3)$ (eV) Final | $\theta^\circ$ | $\theta_1^\circ$ | $\theta_2^\circ$ | $d_1$ ( $a_0$ ) | $d_2$ ( $a_0$ ) |
|------------------------------------------------------------|--------------|-------------------|-------------------|-------------------|-------------------|-------------------------------------------|------------------------------|----------------------------------------------|-------------------------------|----------------|------------------|------------------|-----------------|-----------------|
| $\text{C}-\text{H}(\text{CH}_3)$                           | $\text{C}_a$ | -0.56690          | 0                 | 0                 | 0                 | -152.18259                                | 0.91771                      | -15.39265                                    | -15.20178                     | 79.89          | 101.11           | 43.13            | 1.20367         | 0.15311         |
| $\text{C}-\text{H}(\text{CH}_3)$                           | $\text{C}_c$ | -0.85035          | -0.85035          | -0.56690          | 0                 | -153.88327                                | 0.91771                      | -17.09334                                    | -16.90248                     | 74.42          | 105.58           | 38.84            | 1.24678         | 0.21379         |
| $\text{C}'=\text{H}_a=\text{C}$                            | $\text{C}_c$ | -0.85035          | -0.85035          | -0.56690          | 0                 | -153.88327                                | 0.91771                      | -17.09334                                    | -16.90248                     | 134.24         | 45.76            | 58.98            | 0.75935         | 0.55533         |
| $\text{C}'=\text{H}_c(\text{CH}_3)\text{C}_a=\text{C}$     | $\text{C}_c$ | -0.85035          | -0.85035          | -0.56690          | 0                 | -152.18259                                | 0.91771                      | -15.39265                                    | -15.20178                     | 73.38          | 106.62           | 34.97            | 1.68807         | 0.25279         |
| $\left(\text{C}'=\right)_2\text{C}_a-\text{C}_c\text{H}_3$ | $\text{C}_c$ | -0.56690          | 0                 | 0                 | 0                 | -152.18259                                | 0.91771                      | -17.09334                                    | -16.90247                     | 61.56          | 118.44           | 28.27            | 1.81430         | 0.37901         |
| $\left(\text{C}'=\right)_2\text{C}_c-\text{C}_a\text{H}_3$ | $\text{C}_c$ | -0.56690          | -0.85035          | -0.85035          | 0                 | -153.88328                                | 0.91771                      | -17.09334                                    | -16.90247                     |                |                  |                  |                 |                 |

Table 15.228. The energy parameters (eV) of functional groups of toluene.

| Parameters                     | ${}^3\sigma$<br>$C=C$<br>Group | $CH$ (i)<br>Group       | $C-C$<br>Group  | $CH_3$<br>Group              |
|--------------------------------|--------------------------------|-------------------------|-----------------|------------------------------|
| $f_1$                          | 0.75                           | 1                       |                 |                              |
| $n_1$                          | 2                              | 1                       | 1               | 3                            |
| $n_2$                          | 0                              | 0                       | 0               | 2                            |
| $n_3$                          | 0                              | 0                       | 0               | 0                            |
| $C_1$                          | 0.5                            | 0.75                    | 0.5             | 0.75                         |
| $C_2$                          | 0.85252                        | 1                       | 1               | 1                            |
| $c_1$                          | 1                              | 1                       | 1               | 1                            |
| $c_2$                          | 0.85252                        | 0.91771                 | 0.91771         | 0.91771                      |
| $c_3$                          | 0                              | 1                       | 0               | 0                            |
| $c_4$                          | 3                              | 1                       | 2               | 1                            |
| $c_5$                          | 0                              | 1                       | 0               | 3                            |
| $C_{1o}$                       | 0.5                            | 0.75                    | 0.5             | 0.75                         |
| $C_{2o}$                       | 0.85252                        | 1                       | 1               | 1                            |
| $V_v$ (eV)                     | -101.12679                     | -37.10024               | -29.95792       | -107.32728                   |
| $V_p$ (eV)                     | 20.69825                       | 13.17125                | 9.47952         | 38.92728                     |
| $T$ (eV)                       | 34.31559                       | 11.58941                | 7.27120         | 32.53914                     |
| $V_m$ (eV)                     | -17.15779                      | -5.79470                | -3.63560        | -16.26957                    |
| $E_{AOIHO}$ (eV)               | 0                              | -14.63489               | -15.35946       | -15.56407                    |
| $\Delta E_{H_2MO(AOIHO)}$ (eV) | 0                              | -1.13379                | -0.56690        | 0                            |
| $E_T(AOIHO)$ (eV)              | 0                              | -13.50110               | -14.79257       | -15.56407                    |
| $E_T(H_2MO)$ (eV)              | -63.27075                      | -31.63539               | -31.63537       | -67.69451                    |
| $E_T(atom-atom,msp^3.AO)$ (eV) | -2.26759                       | -0.56690                | -1.13379        | 0                            |
| $E_T(MO)$ (eV)                 | -65.53833                      | -32.20226               | -32.76916       | -67.69450                    |
| $\omega$ ( $10^{15}$ rad / s)  | 49.7272                        | 26.4826                 | 16.2731         | 24.9286                      |
| $E_K$ (eV)                     | 32.73133                       | 17.43132                | 10.71127        | 16.40846                     |
| $\bar{E}_D$ (eV)               | -0.35806                       | -0.26130                | -0.21217        | -0.25352                     |
| $\bar{E}_{Kvib}$ (eV)          | 0.19649<br>[49]                | 0.35532<br>Eq. (13.458) | 0.14940<br>[53] | 0.35532<br>(Eq.<br>(13.458)) |
| $\bar{E}_{osc}$ (eV)           | -0.25982                       | -0.08364                | -0.13747        | -0.22757                     |
| $E_{mag}$ (eV)                 | 0.14803                        | 0.14803                 | 0.14803         | 0.14803                      |
| $E_T(Group)$ (eV)              | -49.54347                      | -32.28590               | -32.90663       | -67.92207                    |
| $E_{initial}(c_1 AOIHO)$ (eV)  | -14.63489                      | -14.63489               | -14.63489       | -14.63489                    |
| $E_{initial}(c_5 AOIHO)$ (eV)  | 0                              | -13.59844               | 0               | -13.59844                    |
| $E_D(Group)$ (eV)              | 5.63881                        | 3.90454                 | 3.63685         | 12.49186                     |

Table 15.229. The total bond energies of toluene calculated using the functional group composition and the energies of Table 15.228 compared to the experimental values [2].

| Formula  | Name    | $C=C$ | $C-H$ (i) | $C-H$ Group | $C-H_3$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|----------|---------|-------|-----------|-------------|---------|-----------------------------------|-------------------------------------|----------------|
| $C_6H_6$ | Toluene | 6     | 5         | 1           | 1       | 69.546                            | 69.546                              | 0.00088        |

Table 15.230. The bond angle parameters of toluene and experimental values [1].  $E_T$  is  $E_T(Atom-atom,exp, AO)$ .

| Atoms of Angle           | $2c'$ Bond 1 ( $a_0$ ) | $2c'$ Bond 2 ( $a_0$ ) | $2c'$ Terminal Atoms ( $a_0$ ) | $E_{T,calc}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{T,calc}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$  | $E_T$ (eV) | $\theta_r$ ( $^\circ$ ) | $\theta_1$ ( $^\circ$ ) | $\theta_2$ ( $^\circ$ ) | Cal. $\theta$ ( $^\circ$ ) | Exp. $\theta$ ( $^\circ$ ) |
|--------------------------|------------------------|------------------------|--------------------------------|---------------------|-------------------------------------------------|---------------------|-------------------------------------------------|--------------|--------------|-------|-------|-------|---------|------------|-------------------------|-------------------------|-------------------------|----------------------------|----------------------------|
| $\angle C'CC$ (aromatic) | 2.62936                | 2.62936                | 4.5585                         | -17.17218           | 34                                              | -17.17218           | 34                                              | 0.79232      | 0.79232      | 1     | 1     | 1     | 0.79232 | -1.85836   |                         |                         |                         | 120.19                     | 120 [50-52] (benzene)      |
| $\angle C'CH$ (aromatic) |                        |                        |                                |                     |                                                 |                     |                                                 |              |              |       |       |       |         |            |                         | 120.19                  |                         | 119.91                     | 120 [50-52] (benzene)      |

## CHLOROBENZENES

Chlorobenzenes have the formula  $C_6H_{6-m}Cl_m$  and comprise the benzene molecule with at least one hydrogen atom replaced by a chlorine atom corresponding to a  $C-Cl$  functional group. The aromatic  $C \equiv C$  and  $C-H$  functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section.

The small differences between energies of ortho, meta, and para-dichlorobenzene is due to differences in the energies of vibration in the transition state that contribute to  $E_{osc}$ . Two types of  $C-Cl$  functional groups can be identified based on symmetry that determine the parameter  $R$  in Eq. (15.48). One corresponds to the special case of 1,3,5 substitution and the other corresponds to other cases of single or multiple substitutions of  $Cl$  for  $H$ . P-dichlorobenzene is representative of the bonding with  $R = a$ . 1,2,3-trichlorobenzene is the particular case wherein is  $R = b$ . Also, beyond the binding of three chlorides  $E_{mag}$  is subtracted for each additional  $Cl$  due to the formation of an unpaired electrons on each  $C-Cl$  bond.

The bond between the chlorine and aromatic ring comprises two  $C-Cl$  functional groups that are solved using the same principles as those used to solve the alkyl chloride functional groups as given in the corresponding section wherein the  $2s$  and  $2p$  AOs of each  $C$  hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and  $Cl$  AO to form a MO permits each participating hybridized orbital to decrease in radius and energy. As in the case of alkyl chlorides,  $c_2$  of Eq. (15.52) for each  $C-Cl$ -bond MO is one, and the energy matching condition is determined by the  $C_2$  parameter given by Eq. (15.111) which is  $C_2(C2sp^3HO \text{ to } Cl) = 0.81317$ . To match energies within the MO that bridges the chlorine AO and aromatic carbon  $C2sp^3$  HO,  $E(AO / HO)$  and  $\Delta E_{H_2MO}(AO / HO)$  in Eq. (15.42) are  $-14.63489 \text{ eV}$  and  $-2.99216 \text{ eV}$ , respectively. The latter matches twice that of the replaced  $C-H$ -bond MO plus  $E_T(atom - atom, msp^3.AO)$ . To match the energies of the functional groups,  $E_T(atom - atom, msp^3.AO)$  of the  $C-Cl$ -bond MO in Eq. (15.53) due to the charge donation from the  $C$  and  $Cl$  atoms to the MO is  $-0.72457 \text{ eV}$  (Eq. (14.151)).

The symbols of the functional groups of chlorobenzenes are given in Table 15.231. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of chlorobenzenes are given in Tables 15.232, 15.233, and 15.234, respectively. The total energy of each chlorobenzene given in Table 15.235 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.234 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_D(\text{Group})$  (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of chlorobenzenes determined using Eqs. (15.79-15.108) are given in Table 15.236.

Table 15.231. The symbols of functional groups of chlorobenzenes.

| Functional Group                                       | Group Symbol          |
|--------------------------------------------------------|-----------------------|
| CC (aromatic bond)                                     | $C \overset{3e}{=} C$ |
| CH (aromatic)                                          | CH (i)                |
| Cl - C (Cl to aromatic bond)                           | C - Cl (a)            |
| Cl - C (Cl to aromatic bond of 1,3,5-trichlorobenzene) | C - Cl (b)            |

Table 15.23.2. The geometrical bond parameters of chlorobenzenes and experimental values [1].

| Parameter                             | $\text{C}=\text{C}$<br>Group | $\text{C}-\text{H}$ (l)<br>Group | $\text{C}-\text{Cl}$ (a)<br>Group | $\text{C}-\text{Cl}$ (b)<br>Group |
|---------------------------------------|------------------------------|----------------------------------|-----------------------------------|-----------------------------------|
| $a$ ( $a_0$ )                         | 1.47348                      | 1.60061                          | 2.20799                           | 2.20799                           |
| $c'$ ( $a_0$ )                        | 1.31468                      | 1.03299                          | 1.64782                           | 1.64782                           |
| Bond Length<br>$2c'$ ( $\text{\AA}$ ) | 1.39140                      | 1.09327                          | 1.74397                           | 1.74397                           |
| Exp. Bond Length<br>( $\text{\AA}$ )  | 1.400<br>(chlorobenzene)     | 1.083<br>(chlorobenzene)         | 1.737<br>(chlorobenzene)          | 1.737<br>(chlorobenzene)          |
| $h, c$ ( $a_0$ )                      | 0.66540                      | 1.2265                           | 1.46967                           | 1.46967                           |
| $e$                                   | 0.89223                      | 0.64537                          | 0.74630                           | 0.74630                           |

Table 15.23.3. The MO to HO intercept geometrical bond parameters of chlorobenzenes.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{mwp}, \text{AO})$ .

| Bond                                                                                                                                     | Atom                | $E_T$<br>(eV)<br>Bond 1 | $E_T$<br>(eV)<br>Bond 2 | $E_T$<br>(eV)<br>Bond 3 | $E_T$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>( $2, sp^3$ )<br>(eV) | $r_{\text{bond}}$<br>( $a_0$ ) | $r_{\text{bond}}$<br>( $a_0$ ) | $E_{\text{bond}}(2, sp^3)$<br>(eV)<br>Final | $E(C2, sp^3)$<br>(eV)<br>Final | $\theta^1$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | $d_1$<br>( $a_0$ ) | $d_2$<br>( $a_0$ ) |
|------------------------------------------------------------------------------------------------------------------------------------------|---------------------|-------------------------|-------------------------|-------------------------|-------------------------|------------------------------------------------|--------------------------------|--------------------------------|---------------------------------------------|--------------------------------|----------------------------|----------------------------|----------------------------|--------------------|--------------------|
| $\text{C}-\text{H}(\text{C}, \text{H})$                                                                                                  | $\text{C}_\text{H}$ | -0.85035                | -0.85035                | -0.56690                | 0                       | -153.88327                                     | 0.91771                        | 0.79597                        | -17.09334                                   | -16.59248                      | 74.42                      | 105.58                     | 38.84                      | 1.24678            | 0.21379            |
| $\text{C}=\text{HC}_\text{H}=\text{C}$                                                                                                   | $\text{C}_\text{H}$ | -0.85035                | -0.85035                | -0.56690                | 0                       | -153.88327                                     | 0.91771                        | 0.79597                        | -17.09334                                   | -16.59248                      | 134.24                     | 45.76                      | 58.98                      | 0.75935            | 0.55533            |
| $\text{C}=\text{C}_\text{H}-\text{Cl}$                                                                                                   | $\text{C}_\text{H}$ | -0.36229                | -0.85035                | -0.85035                | 0                       | -153.67867                                     | 0.91771                        | 0.80561                        | -16.88873                                   | -16.69786                      | 73.32                      | 106.68                     | 31.67                      | 1.87911            | 0.23129            |
| $\text{C}=\text{C}_\text{H}-\text{Cl}$                                                                                                   | $\text{Cl}$         | -0.36229                | 0                       | 0                       | 0                       |                                                | 1.05158                        | 0.89582                        | 15.18804                                    |                                | 82.92                      | 97.08                      | 37.22                      | 1.75824            | 0.11042            |
| $\text{C}_\text{H}=\text{C}(\text{Cl})\text{C}_\text{H}=\text{C}_\text{H}$<br>( $\text{C}_\text{H}$ bound to $\text{H}$ or $\text{Cl}$ ) | $\text{C}_\text{H}$ | -0.36229                | -0.85035                | -0.85035                | 0                       | -153.67867                                     | 0.91771                        | 0.80561                        | -16.88873                                   | -16.69786                      | 134.65                     | 45.35                      | 59.47                      | 0.74854            | 0.56614            |



TABLE 10-10: The energy parameters (eV) of functional groups of chlorobenzenes.

| Parameters                                      | $\overset{\text{ar}}{\text{C}}=\text{C}$<br>Group | CH (i)<br>Group         | C - Cl (a)<br>Group | C - Cl (b)<br>Group |
|-------------------------------------------------|---------------------------------------------------|-------------------------|---------------------|---------------------|
| $f_1$                                           | 0.75                                              | 1                       |                     |                     |
| $n_1$                                           | 2                                                 | 1                       | 1                   | 1                   |
| $n_2$                                           | 0                                                 | 0                       | 0                   | 0                   |
| $n_3$                                           | 0                                                 | 0                       | 0                   | 0                   |
| $C_1$                                           | 0.5                                               | 0.75                    | 0.5                 | 0.5                 |
| $C_2$                                           | 0.85252                                           | 1                       | 0.81317             | 0.81317             |
| $c_1$                                           | 1                                                 | 1                       | 1                   | 1                   |
| $c_2$                                           | 0.85252                                           | 0.91771                 | 1                   | 1                   |
| $c_3$                                           | 0                                                 | 1                       | 0                   | 0                   |
| $c_4$                                           | 3                                                 | 1                       | 2                   | 2                   |
| $c_5$                                           | 0                                                 | 1                       | 0                   | 0                   |
| $C_{1o}$                                        | 0.5                                               | 0.75                    | 0.5                 | 0.5                 |
| $C_{2o}$                                        | 0.85252                                           | 1                       | 0.81317             | 0.81317             |
| $V_e$ (eV)                                      | -101.12679                                        | -37.10024               | -31.85648           | -31.85648           |
| $V_p$ (eV)                                      | 20.69825                                          | 13.17125                | 8.25686             | 8.25686             |
| $T$ (eV)                                        | 34.31559                                          | 11.58941                | 7.21391             | 7.21391             |
| $V_m$ (eV)                                      | -17.15779                                         | -5.79470                | -3.60695            | -3.60695            |
| $E(\text{ar})$ (eV)                             | 0                                                 | -14.63489               | -14.63489           | -14.63489           |
| $\Delta E_{H_2MO}(\text{ar})$ (eV)              | 0                                                 | -1.13379                | -2.99216            | -2.99216            |
| $E_T(\text{ar})$ (eV)                           | 0                                                 | -13.50110               | -11.64273           | -11.64273           |
| $E_T(H_2MO)$ (eV)                               | -63.27075                                         | -31.63539               | -31.63539           | -31.63539           |
| $E_T(\text{atom} - \text{atom}, msp^3.AO)$ (eV) | -2.26759                                          | -0.56690                | -0.72457            | -0.72457            |
| $E_T(MO)$ (eV)                                  | -65.53833                                         | -32.20226               | -32.35994           | -32.35994           |
| $\omega$ ( $10^{15}$ rad / s)                   | 49.7272                                           | 26.4826                 | 8.03459             | 14.7956             |
| $E_K$ (eV)                                      | 32.73133                                          | 17.43132                | 5.28851             | 9.73870             |
| $\bar{E}_D$ (eV)                                | -0.35806                                          | -0.26130                | -0.14722            | -0.19978            |
| $\bar{E}_{Kvib}$ (eV)                           | 0.19649<br>[49]                                   | 0.35532<br>Eq. (13.458) | 0.08059<br>[12]     | 0.08059<br>[12]     |
| $\bar{E}_{osc}$ (eV)                            | -0.25982                                          | -0.08364                | -0.10693            | -0.15949            |
| $E_{mag}$ (eV)                                  | 0.14803                                           | 0.14803                 | 0.14803             | 0.14803             |
| $E_T(\text{Group})$ (eV)                        | -49.54347                                         | -32.28590               | -32.46687           | -32.51943           |
| $E_{initial}(e_1 \text{ ar})$ (eV)              | -14.63489                                         | -14.63489               | -14.63489           | -14.63489           |
| $E_{initial}(e_3 \text{ ar})$ (eV)              | 0                                                 | -13.59844               | 0                   | 0                   |
| $E_D(\text{Group})$ (eV)                        | 5.63881                                           | 3.90454                 | 3.19709             | 3.24965             |

Table 15.235. The total bond energies of chlorobenzenes calculated using the functional group composition and the energies of Table 15.234 compared to the experimental values [2]. The magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_b$  values based on composition is given by (15.58).

| Formula      | Name                   | $C \equiv C$ | $CH$ (t) | $C-C$ (a) | $C-C$ (b) | $E_{mag}$ | Calculated Total Bond Energy (kJ) | Experimental Total Bond Energy (kJ) | Relative Error |
|--------------|------------------------|--------------|----------|-----------|-----------|-----------|-----------------------------------|-------------------------------------|----------------|
| $C_6H_5Cl$   | Chlorobenzene          | 6            | 5        | 1         | 0         | 0         | 56.5263                           | 56.581                              | 0.00051        |
| $C_6H_4Cl_2$ | m-dichlorobenzene      | 6            | 4        | 2         | 0         | 0         | 55.84518                          | 55.832                              | 0.00012        |
| $C_6H_3Cl_3$ | 1,2,3-trichlorobenzene | 6            | 3        | 3         | 0         | 0         | 55.13775                          | 55.077                              | -0.00111       |
| $C_6H_2Cl_4$ | 1,3,5-trichlorobenzene | 6            | 3        | 0         | 1         | 0         | 55.29542                          | 55.255                              | -0.00079       |
| $C_6Cl_6$    | Hexachlorobenzene      | 6            | 0        | 6         | 0         | 3         | 52.57130                          | 52.477                              | -0.00179       |

Table 15.236. The bond angle parameters of chlorobenzenes and experimental values [1].  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{mwp}, \text{AO})$ .

| Atoms/Angle                       | $2C^1$<br>Bond 1<br>( $\alpha_1$ ) | $2C^1$<br>Bond 2<br>( $\alpha_2$ ) | $2C^1$<br>Terminal<br>Atom<br>( $\alpha_3$ ) | $E_{r,calc}$<br>Atom 1 | Atom 1<br>Hybridization<br>Designation<br>(Table 15.3.A) | $E_{r,calc}$<br>Atom 2 | Atom 2<br>Hybridization<br>Designation<br>(Table 15.3.A) | $\zeta_1$<br>Atom 1 | $\zeta_2$<br>Atom 2 | $\zeta_1$ | $\zeta_2$ | $\zeta_1$ | $\zeta_2$ | $\zeta_1$ | $\zeta_2$ | $E_r$<br>(eV) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | $\theta_3$<br>( $^\circ$ ) | Cal. $\theta$<br>( $^\circ$ ) | Exp. $\theta$<br>( $^\circ$ )                                                                            |
|-----------------------------------|------------------------------------|------------------------------------|----------------------------------------------|------------------------|----------------------------------------------------------|------------------------|----------------------------------------------------------|---------------------|---------------------|-----------|-----------|-----------|-----------|-----------|-----------|---------------|----------------------------|----------------------------|----------------------------|-------------------------------|----------------------------------------------------------------------------------------------------------|
| $\angle C \equiv C$<br>(aromatic) | 2.62936                            | 2.62936                            | 4.5985                                       | -17.17218              | 34                                                       | -17.17218              | 34                                                       | 0.79232             | 0.79232             | 1         | 1         | 1         | 1         | 0.79232   |           | -1.85836      |                            |                            |                            | 120.19                        | 120<br>chlorobenzene<br>121.7<br>( $\angle C \equiv C$ )(C)<br>chlorobenzene<br>120 [50-52]<br>(benzene) |
| $\angle C \equiv C$<br>(aromatic) |                                    |                                    |                                              |                        |                                                          |                        |                                                          |                     |                     |           |           |           |           |           |           |               |                            |                            |                            | 120.19                        | 120 [50-52]<br>(benzene)                                                                                 |

## PHENOL

Phenol has the formula  $C_6H_6O$  and comprises the benzene molecule with one hydrogen atom replaced by a hydroxyl corresponding to an  $OH$  functional group and a  $C-O$  functional group. The aromatic  $C \equiv C^{3e}$  and  $C-H$  functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The  $OH$  functional group is the same as that of alcohols given in the corresponding section.

The bond between the hydroxyl and aromatic ring comprises a  $C-O$  functional group that is are solved using the same principles as those used to solve the alcohol functional groups wherein the  $2s$  and  $2p$  AOs of each  $C$  hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and  $O$  AO to form a MO permits each participating hybridized orbital to decrease in radius and energy. In aryl alcohols, the aromatic  $C2sp^3$  HO has a hybridization factor of 0.85252 (Eq. (15.143)) with an initial energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)) and the  $O$  AO has an energy of  $E(O) = -13.61806 \text{ eV}$ . To meet the equipotential condition of the union of the  $C-O$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the  $C-O$ -bond MO given by Eqs. (15.68) and (15.70) is

$$\begin{aligned} c_2(\text{aryl}C2sp^3HO \text{ to } O) &= \frac{E(O)}{E(C, 2sp^3)} c_2(\text{aryl}C2sp^3HO) \\ &= \frac{-13.61806 \text{ eV}}{-14.63489 \text{ eV}} (0.85252) \\ &= 0.79329 \end{aligned} \quad (15.150)$$

$E_r(\text{atom} - \text{atom}, msp^3.AO)$  of the  $C-O$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $O$  atoms to the MO is  $-1.49608 \text{ eV}$ . It is based on the energy match between the  $OH$  group and the  $C2sp^3$  HO of an aryl group and is given by the linear combination of  $-0.92918 \text{ eV}$  (Eq. (14.513)) and  $-1.13379 \text{ eV}$  (Eq. (14.247)), respectively.

The symbols of the functional groups of phenol are given in Table 15.237. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of phenol are given in Tables 15.238, 15.239, and 15.240, respectively. The total energy of phenol given in Table 15.241 was calculated as the sum over the integer multiple of each  $E_p(\text{group})$  of Table 15.240

corresponding to functional-group composition of the molecule. The bond angle parameters of phenol determined using Eqs. (15.79-15.108) are given in Table 15.242.

Table 15.237. The symbols of functional groups of phenol.

| Functional Group   | Group Symbol        |
|--------------------|---------------------|
| CC (aromatic bond) | $\overset{3e}{C}=C$ |
| CH (aromatic)      | CH (i)              |
| Aryl C-O           | C-O (a)             |
| OH group           | OH                  |

5

Table 15.238. The geometrical bond parameters of phenol and experimental values [1].

| Parameter                               | $\overset{3e}{C}=C$<br>Group | CH (i)<br>Group   | C-O (a)<br>Group  | OH<br>Group       |
|-----------------------------------------|------------------------------|-------------------|-------------------|-------------------|
| $a (a_0)$                               | 1.47348                      | 1.60061           | 1.68220           | 1.26430           |
| $c' (a_0)$                              | 1.31468                      | 1.03299           | 1.29700           | 0.91808           |
| Bond Length<br>$2c' (\text{\AA})$       | 1.39140                      | 1.09327           | 1.37268           | 0.971651          |
| Exp. Bond<br>Length<br>( $\text{\AA}$ ) | 1.397 avg.<br>(phenol)       | 1.084<br>(phenol) | 1.364<br>(phenol) | 0.956<br>(phenol) |
| $b, c (a_0)$                            | 0.66540                      | 1.22265           | 1.07126           | 0.86925           |
| $e$                                     | 0.89223                      | 0.64537           | 0.77101           | 0.72615           |

Table 15.239. The MO to HO intercept geometrical bond parameters of phenol.  $E_i$  is  $E_i(\text{atom} - \text{atom}, \text{mp}, A(0))$ .

| Bond               | Atom  | $E_1$<br>(eV) | $E_2$<br>(eV) | $E_3$<br>(eV) | $E_4$<br>(eV) | Final Total<br>Energy<br>( $C_{2sp}^3$ )<br>(eV) | $r_{\text{bond}}$<br>( $a_0$ ) | $r_{\text{bond}}$<br>( $a_0$ ) | $E_{\text{inter}}(C_{2sp}^3)$<br>(eV)<br>Final | $E(C_{2sp}^3)$<br>(eV)<br>Final | $\theta$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | $d_1$<br>( $a_0$ ) | $d_2$<br>( $a_0$ ) |
|--------------------|-------|---------------|---------------|---------------|---------------|--------------------------------------------------|--------------------------------|--------------------------------|------------------------------------------------|---------------------------------|--------------------------|----------------------------|----------------------------|--------------------|--------------------|
| $C-H$ ( $C_1H$ )   | $C_1$ | -0.85035      | -0.85035      | -0.56690      | 0             | -153.88327                                       | 0.91771                        | 0.79597                        | -17.09334                                      | -16.90248                       | 74.42                    | 105.58                     | 38.84                      | 1.2678             | 0.21379            |
| $C_1=$<br>$C_2O-H$ | $O$   | -0.74804      | 0             | 0             | 0             |                                                  | 1.00000                        | 0.87363                        | -15.57379                                      |                                 | 115.79                   | 64.21                      | 64.82                      | 0.53799            | 0.38009            |
| $C_1=$<br>$C_2O-H$ | $C_2$ | -0.74804      | -0.85035      | -0.85035      | 0             | -154.06442                                       | 0.91771                        | 0.78762                        | -17.27448                                      | -17.08362                       | 100.00                   | 80.00                      | 46.39                      | 1.16026            | 0.13674            |
| $C_1=$<br>$C_2O-H$ | $O$   | -0.74804      | 0             | 0             | 0             |                                                  | 1.00000                        | 0.87363                        | 15.57379                                       |                                 | 106.51                   | 73.49                      | 51.43                      | 1.04871            | 0.24829            |
| $C_1=$<br>$C_2O-H$ | $C_1$ | -0.74804      | -0.85035      | -0.85035      | 0             | -154.06442                                       | 0.91771                        | 0.78762                        | -17.27448                                      | -17.08362                       | 133.88                   | 46.12                      | 58.55                      | 0.76870            | 0.34598            |
| $C_1=$<br>$C_2O-H$ | $C_1$ | -0.85035      | -0.85035      | -0.56690      | 0             | -153.88327                                       | 0.91771                        | 0.79597                        | -17.09334                                      | -16.90248                       | 134.24                   | 45.76                      | 58.98                      | 0.73955            | 0.55553            |

Table 15.240. The energy parameters (eV) of functional groups of phenol.

| Parameters                               | $\overset{3e}{C=C}$<br>Group | CH (i)<br>Group         | C-O (a)<br>Group | OH<br>Group        |
|------------------------------------------|------------------------------|-------------------------|------------------|--------------------|
| $f_1$                                    | 0.75                         | 1                       |                  |                    |
| $n_1$                                    | 2                            | 1                       | 1                | 1                  |
| $n_2$                                    | 0                            | 0                       | 0                | 0                  |
| $n_3$                                    | 0                            | 0                       | 0                | 0                  |
| $C_1$                                    | 0.5                          | 0.75                    | 0.5              | 0.75               |
| $C_2$                                    | 0.85252                      | 1                       | 1                | 1                  |
| $c_1$                                    | 1                            | 1                       | 1                | 0.75               |
| $c_2$                                    | 0.85252                      | 0.91771                 | 0.79329          | 1                  |
| $c_3$                                    | 0                            | 1                       | 0                | 1                  |
| $c_4$                                    | 3                            | 1                       | 2                | 1                  |
| $c_5$                                    | 0                            | 1                       | 0                | 1                  |
| $C_{1o}$                                 | 0.5                          | 0.75                    | 0.5              | 0.75               |
| $C_{2o}$                                 | 0.85252                      | 1                       | 1                | 1                  |
| $V_e$ (eV)                               | -101.12679                   | -37.10024               | -34.04658        | -40.92709          |
| $V_p$ (eV)                               | 20.69825                     | 13.17125                | 10.49024         | 14.81988           |
| $T$ (eV)                                 | 34.31559                     | 11.58941                | 10.11966         | 16.18567           |
| $V_m$ (eV)                               | -17.15779                    | -5.79470                | -5.05983         | -8.09284           |
| $E(\lambda O I H O)$ (eV)                | 0                            | -14.63489               | -14.63489        | -13.6181           |
| $\Delta E_{H_2MO}(\lambda O I H O)$ (eV) | 0                            | -1.13379                | -1.49608         | 0                  |
| $E_T(\lambda O I H O)$ (eV)              | 0                            | -13.50110               | -13.13881        | -13.6181           |
| $E_T(H_2MO)$ (eV)                        | -63.27075                    | -31.63539               | -31.63532        | -31.63247          |
| $E_T(atom - atom, msp^3 AO)$ (eV)        | -2.26759                     | -0.56690                | -1.49608         | 0                  |
| $E_T(MO)$ (eV)                           | -65.53833                    | -32.20226               | -33.13145        | -31.63537          |
| $\omega$ ( $10^{15}$ rad / s)            | 49.7272                      | 26.4826                 | 13.3984          | 44.1776            |
| $E_K$ (eV)                               | 32.73133                     | 17.43132                | 8.81907          | 29.07844           |
| $\bar{E}_D$ (eV)                         | -0.35806                     | -0.26130                | -0.19465         | -0.33749           |
| $\bar{E}_{Kvib}$ (eV)                    | 0.19649<br>[49]              | 0.35532<br>Eq. (13.458) | 0.12808<br>[19]  | 0.46311<br>[17-18] |
| $\bar{E}_{osc}$ (eV)                     | -0.25982                     | -0.08364                | -0.13061         | -0.10594           |
| $E_{mag}$ (eV)                           | 0.14803                      | 0.14803                 | 0.14803          | 0.11441            |
| $E_T(Group)$ (eV)                        | -49.54347                    | -32.28590               | -33.26206        | -31.74130          |
| $E_{minal}(c_1 \lambda O I H O)$ (eV)    | -14.63489                    | -14.63489               | -14.63489        | -13.6181           |
| $E_{minal}(c_2 \lambda O I H O)$ (eV)    | 0                            | -13.59844               | 0                | -13.59844          |
| $E_D(Group)$ (eV)                        | 5.63881                      | 3.90454                 | 3.99228          | 4.41035            |

Table 15.241. The total bond energies of phenol calculated using the functional group composition and the energies of Table 15.240 compared to the experimental values [2].

| Formula   | Name   | $C^x$ | $(^1H)$ | $(^1H)$ | $(^1H)$ | Calculated             | Experimental           | Relative |
|-----------|--------|-------|---------|---------|---------|------------------------|------------------------|----------|
| $C_6H_6O$ | Phenol | 6     | 5       | 1       | 1       | Total Bond Energy (kJ) | Total Bond Energy (kJ) | Error    |
|           |        |       |         |         |         | 61.5817                | 61.704                 | -0.00087 |

Table 15.242. The bond angle parameters of phenol and experimental values [1].  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{amp}^2, \text{Å}^2)$ .

| Atoms of Angle                     | $2\sigma^1$<br>Bond 1<br>( $a_1$ ) | $2\sigma^1$<br>Bond 2<br>( $a_2$ ) | $2\sigma^1$<br>Terminal<br>Atoms<br>( $a_3$ ) | $E_T$<br>Atom 1 | Atom 1<br>Hybridization<br>Designation<br>(Table 15.3.A) | $E_T$<br>Atom 2 | Atom 2<br>Hybridization<br>Designation<br>(Table 15.3.A) | $c_1$<br>Atom 1 | $c_2$<br>Atom 2 | $c_3$ | $c_4$ | $c_5$ | $c_6$   | $E_T$<br>(eV) | $\theta_1$<br>(°) | $\theta_2$<br>(°) | Col. $\theta$<br>(°) | Exp. $\theta$<br>(°)     |
|------------------------------------|------------------------------------|------------------------------------|-----------------------------------------------|-----------------|----------------------------------------------------------|-----------------|----------------------------------------------------------|-----------------|-----------------|-------|-------|-------|---------|---------------|-------------------|-------------------|----------------------|--------------------------|
| $\angle C_1 C_2 C_3$<br>(aromatic) | 2.62956                            | 2.62956                            | 4.5385                                        | -17.17218       | 34                                                       | -17.17218       | 34                                                       | 0.79232         | 0.79232         | 1     | 1     | 1     | 0.79232 | -1.85356      |                   |                   | 120.19               | 120 [50-52]<br>(benzene) |
| $\angle C_1 C_2 H$<br>(aromatic)   |                                    |                                    |                                               |                 |                                                          |                 |                                                          |                 |                 |       |       |       |         |               | 120.19            |                   | 119.91               | 120 [50-52]<br>(benzene) |
| $\angle C_1 O H$                   | 2.59999                            | 1.85016                            | 3.6815                                        | -14.82575       | 1                                                        | -14.82575       | 1                                                        | 1               | 0.91771         | 0.75  | 1     | 0.75  | 0.91771 | 0             |                   |                   | 109.84               | 109.2<br>(phenol)        |

## ANILINE

Aniline and methyl aniline have the formula  $C_6H_7N$  and  $C_7H_9N$ , respectively. They comprise the benzene and toluene molecules with one hydrogen atom replaced by an amino group corresponding to an  $NH_2$  functional group and a  $C-N$  functional group. The aromatic  $C=C$  and  $C-H$  functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The  $C-C$  and  $CH_3$  functional groups of methyl anilines are equivalent to those of toluene given in the corresponding section.

The aryl amino ( $NH_2$ ) functional group was solved using the procedure given in the Dihydrogen Nitride ( $NH_2$ ) section. Using the results of Eqs. (13.245-13.368), the aryl amino parameters in Eq. (15.51) are  $n_1 = 2$ ,  $C_1 = 0.75$ ,  $C_2 = 0.93613$  (Eqs. (13.248-13.249)),  $C_{1o} = 1.5$ , and  $c_1 = 0.75$ . In the determination of the hybridization factor  $c_2$  of Eq. (15.52) for the  $N-H$ -bond MO of aryl amines, the  $C2sp^3$  HO of the  $C-NH_2$ -bond MO has an energy of  $E(C, 2sp^3) = -15.76868 \text{ eV}$  (Eq. (15.18) corresponding to  $s = 2$  in Eqs. (15.18-15.20), and the  $N$  AO has an energy of  $E(N) = -14.53414 \text{ eV}$ . To meet the equipotential condition of the union of the  $N-H$   $H_2$ -type-ellipsoidal-MO with the  $C2sp^3$  HO, the hybridization factor  $c_2$  given by Eq. (15.68) is

$$c_2(H \text{ to aniline } N) = \frac{E(N)}{E(C, 2sp^3)} = \frac{-14.53414 \text{ eV}}{-15.76868 \text{ eV}} = 0.92171 \quad (15.151)$$

The bond between the amino and aromatic ring comprises a  $C-N$  functional group that is the same as that of  $2^\circ$  amines (methylene) except that the energies corresponding to oscillation in the transition state are those of aniline. The group is solved using the same principles as those used to solve the primary and secondary-amine functional groups wherein the  $2s$  and  $2p$  AOs of each  $C$  hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and  $N$  AO to form a MO permits each participating hybridized orbital to decrease in radius and energy. The hybridization is determined in a similar manner to that of the  $C-O$  group of phenol. In anilines, the aromatic  $C2sp^3$  HO has a hybridization factor of 0.85252 (Eq. (15.143)) with an initial energy of  $E(C, 2sp^3) = -14.63489 \text{ eV}$  (Eq. (15.25)) and the  $N$  AO has an energy



of  $E(N) = -14.53414 \text{ eV}$ . To meet the equipotential condition of the union of the  $C-O$   $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.51) for the  $C-O$ -bond MO given by Eqs. (15.68) and (15.70) is

$$\begin{aligned} c_2(\text{aryl}C2sp^3HO \text{ to } N) &= \frac{E(N)}{E(C,2sp^3)} c_2(\text{aryl}C2sp^3HO) \\ &= \frac{-14.53414 \text{ eV}}{-14.63489 \text{ eV}} (0.85252) \\ &= 0.84665 \end{aligned} \quad (15.152)$$

5  $E_r(\text{atom-atom}, msp^3.AO)$  of the  $C-N$ -bond MO in Eq. (15.52) due to the charge donation from the  $C$  and  $N$  atoms to the MO is  $-1.13379 \text{ eV}$  (Eq. (14.247)). It is based on the energy

match between the  $NH_2$  group and the  $C2sp^3$  HO of the aryl group and is twice that of the aryl  $C-H$  group that it replaces.

10 The symbols of the functional groups of aniline and methyl-substituted anilines are given in Table 15.243. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aniline and methyl-substituted anilines are given in Tables 15.244, 15.245, and 15.246, respectively. The total energy of each aniline and methyl-substituted aniline given in  
15 Table 15.247 was calculated as the sum over the integer multiple of each  $E_p(\text{Group})$  of Table 15.246 corresponding to functional-group composition of the molecule. The bond angle parameters of aniline and methyl-substituted anilines determined using Eqs. (15.79-15.108) are given in Table 15.248.

20 Table 15.243. The symbols of functional groups of aniline and methyl-substituted anilines.

| Functional Group                       | Group Symbol        |
|----------------------------------------|---------------------|
| CC (aromatic bond)                     | $\overset{3e}{C=C}$ |
| CH (aromatic)                          | $CH$ (i)            |
| Aryl C-N                               | $C-N$ (a)           |
| $NH_2$ group                           | $NH_2$              |
| $C_a - C_b$ ( $CH_3$ to aromatic bond) | $C-C$ (a)           |
| $CH_3$ group                           | $C-H$ ( $CH_3$ )    |

Table 15.244. The geometrical bond parameters of aniline and methyl-substituted anilines and experimental values [1].

| Parameter                     | C=C Group           | C-H (i) Group  | C-N (a) Group   | NH <sub>2</sub> Group | C-H (CH <sub>3</sub> ) Group |
|-------------------------------|---------------------|----------------|-----------------|-----------------------|------------------------------|
| $a$ (Å)                       | 1.47348             | 1.00061        | 1.81158         | 1.24428               | 2.06004                      |
| $c'$ (Å)                      | 1.31468             | 1.03299        | 1.34595         | 0.94134               | 1.04856                      |
| Bond Length<br>$2c'$ (Å)      | 1.39140             | 1.09327        | 1.42449         | 0.98627               | 1.10974                      |
| Exp. Bond Length (phenol) (Å) | 1.397 avg. (phenol) | 1.084 (phenol) | 1.431 (aniline) | 0.998 (aniline)       | 1.11 (avg.) (toluene)        |
| $b_1 c$ (Å)                   | 0.66540             | 1.22265        | 1.21254         | 0.81370               | 1.47774                      |
| $e$                           | 0.89223             | 0.64537        | 0.74297         | 0.75653               | 0.63380                      |

5 Table 15.245. The MO to HO intercept geometrical bond parameters of aniline and methyl-substituted anilines.  $E_r$  is  $E_r$  (atom-atom, msp, AC).

| Bond                                                                         | Atom           | $E_r$ (eV) Bond 1 | $E_r$ (eV) Bond 2 | $E_r$ (eV) Bond 3 | $E_r$ (eV) Bond 4 | Final Total Energy (eV) | $r_{\text{final}}$ (Å) | $r_{\text{final}}$ (Å) | $E_{\text{atom}}(C2sp^2)$ (eV) Final | $E(C2sp^2)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ (Å) | $d_2$ (Å) |
|------------------------------------------------------------------------------|----------------|-------------------|-------------------|-------------------|-------------------|-------------------------|------------------------|------------------------|--------------------------------------|------------------------|---------------|----------------|----------------|-----------|-----------|
| C-H (C <sub>1</sub> H)                                                       | C <sub>1</sub> | -0.85035          | -0.85035          | -0.56690          | 0                 | -153.88328              | 0.91771                | 0.79597                | -17.09334                            | -16.90248              | 74.42         | 105.58         | 38.84          | 1.24678   | 0.21379   |
| C-H (C <sub>1</sub> H <sub>3</sub> )                                         | C <sub>1</sub> | -0.56690          | 0                 | 0                 | 0                 | -152.18259              | 0.91771                | 0.88392                | -15.39265                            | -15.20178              | 79.89         | 101.11         | 43.13          | 1.20567   | 0.13511   |
| C <sub>1</sub> =C <sub>2</sub> C <sub>1</sub> NH-H                           | N              | -0.56690          | 0                 | 0                 | 0                 |                         | 0.93084                | 0.88392                | -15.39265                            |                        | 121.74        | 58.26          | 67.49          | 0.47034   | 0.46500   |
| C <sub>1</sub> =C <sub>2</sub> C <sub>1</sub> -NH <sub>2</sub>               | C <sub>1</sub> | -0.56690          | -0.85035          | -0.85035          | 0                 | -153.88328              | 0.91771                | 0.79597                | -17.09334                            | -16.90248              | 88.49         | 91.51          | 41.01          | 1.36696   | 0.02101   |
| C <sub>1</sub> =C <sub>2</sub> C <sub>1</sub> -NH <sub>2</sub>               | N              | -0.56690          | 0                 | 0                 | 0                 |                         | 0.93084                | 0.88392                | -15.39265                            |                        | 96.32         | 83.68          | 46.43          | 1.24859   | 0.09736   |
| C <sub>1</sub> =C <sub>2</sub> C <sub>1</sub> -C <sub>6</sub> H <sub>5</sub> | C <sub>1</sub> | -0.56690          | 0                 | 0                 | 0                 | -152.18259              | 0.91771                | 0.88392                | -15.39265                            | -15.20178              | 73.38         | 106.62         | 34.97          | 1.08807   | 0.23279   |
| C <sub>1</sub> =C <sub>2</sub> C <sub>1</sub> -C <sub>6</sub> H <sub>5</sub> | C <sub>1</sub> | -0.56690          | -0.85035          | -0.85035          | 0                 | -153.88328              | 0.91771                | 0.79597                | -17.09334                            | -16.90247              | 61.56         | 118.44         | 28.27          | 1.81430   | 0.37901   |
| C <sub>1</sub> =HC <sub>2</sub> C <sub>1</sub>                               | C <sub>1</sub> | -0.85035          | -0.85035          | -0.56690          | 0                 | -153.88327              | 0.91771                | 0.79597                | -17.09334                            | -16.90248              | 134.24        | 45.76          | 58.98          | 0.75855   | 0.25553   |

Table 15.246. The energy parameters (eV) of functional groups of aniline and methyl-substituted anilines.

| Parameters                                                    | $\overset{\text{3e}}{\text{C}}=\text{C}$<br>Group | CH (i)<br>Group         | C – N (a)<br>Group | NH <sub>2</sub><br>Group | C – C (a)<br>Group | CH <sub>3</sub><br>Group  |
|---------------------------------------------------------------|---------------------------------------------------|-------------------------|--------------------|--------------------------|--------------------|---------------------------|
| $f_1$                                                         | 0.75                                              | 1                       |                    |                          |                    |                           |
| $n_1$                                                         | 2                                                 | 1                       | 1                  | 2                        | 1                  | 3                         |
| $n_2$                                                         | 0                                                 | 0                       | 0                  | 0                        | 0                  | 2                         |
| $n_3$                                                         | 0                                                 | 0                       | 0                  | 1                        | 0                  | 0                         |
| $C_1$                                                         | 0.5                                               | 0.75                    | 0.5                | 0.75                     | 0.5                | 0.75                      |
| $C_2$                                                         | 0.85252                                           | 1                       | 1                  | 0.93613                  | 1                  | 1                         |
| $c_1$                                                         | 1                                                 | 1                       | 1                  | 0.75                     | 1                  | 1                         |
| $c_2$                                                         | 0.85252                                           | 0.91771                 | 0.84665            | 0.92171                  | 0.91771            | 0.91771                   |
| $c_3$                                                         | 0                                                 | 1                       | 0                  | 0                        | 0                  | 0                         |
| $c_4$                                                         | 3                                                 | 1                       | 2                  | 1                        | 2                  | 1                         |
| $c_5$                                                         | 0                                                 | 1                       | 0                  | 2                        | 0                  | 3                         |
| $C_{1a}$                                                      | 0.5                                               | 0.75                    | 0.5                | 1.5                      | 0.5                | 0.75                      |
| $C_{2a}$                                                      | 0.85252                                           | 1                       | 1                  | 1                        | 1                  | 1                         |
| $V_e$ (eV)                                                    | -101.12679                                        | -37.10024               | -32.76465          | -78.97795                | -29.95792          | -107.32728                |
| $V_p$ (eV)                                                    | 20.69825                                          | 13.17125                | 10.10870           | 28.90735                 | 9.47952            | 38.92728                  |
| $T$ (eV)                                                      | 34.31559                                          | 11.58941                | 9.04312            | 31.73641                 | 7.27120            | 32.53914                  |
| $V_m$ (eV)                                                    | -17.15779                                         | -5.79470                | -4.52156           | -15.86820                | -3.63560           | -16.26957                 |
| $E_{\text{AOIHO}}$ (eV)                                       | 0                                                 | -14.63489               | -14.63489          | -14.53414                | -15.35946          | -15.56407                 |
| $\Delta E_{\text{H}_2\text{MO}}$ (AOIHO) (eV)                 | 0                                                 | -1.13379                | -1.13379           | 0                        | -0.56690           | 0                         |
| $E_T$ (AOIHO) (eV)                                            | 0                                                 | -13.50110               | -13.50110          | -14.53414                | -14.79257          | -15.56407                 |
| $E(n, \text{AOIHO})$ (eV)                                     | 0                                                 | 0                       | 0                  | -14.53414                | 0                  | 0                         |
| $E_T(\text{H}_2\text{MO})$ (eV)                               | -63.27075                                         | -31.63539               | -31.63549          | -48.73654                | -31.63537          | -67.69451                 |
| $E_T(\text{atom} - \text{atom}, \text{msp}^3 \text{AO})$ (eV) | -2.26759                                          | -0.56690                | -1.13379           | 0                        | -1.13379           | 0                         |
| $E_T(\text{MO})$ (eV)                                         | -65.53833                                         | -32.20226               | -32.76916          | -48.73660                | -32.76916          | -67.69450                 |
| $\omega$ ( $10^{15}$ rad / s)                                 | 49.7272                                           | 26.4826                 | 11.9890            | 68.9812                  | 16.2731            | 24.9286                   |
| $E_K$ (eV)                                                    | 32.73133                                          | 17.43132                | 7.89138            | 45.40465                 | 10.71127           | 16.40846                  |
| $\bar{E}_D$ (eV)                                              | -0.35806                                          | -0.26130                | -0.18211           | -0.42172                 | -0.21217           | -0.25352                  |
| $\bar{E}_{\text{Kvib}}$ (eV)                                  | 0.19649<br>[49]                                   | 0.35532<br>Eq. (13.458) | 0.15498<br>[54]    | 0.40929<br>[22]          | 0.14940<br>[53]    | 0.35532<br>(Eq. (13.458)) |
| $\bar{E}_{\text{osc}}$ (eV)                                   | -0.25982                                          | -0.08364                | -0.10462           | -0.21708                 | -0.13747           | -0.22757                  |
| $E_{\text{mag}}$ (eV)                                         | 0.14803                                           | 0.14803                 | 0.14803            | 0.14803                  | 0.14803            | 0.14803                   |
| $E_T(\text{Group})$ (eV)                                      | -49.54347                                         | -32.28590               | -32.87379          | -49.17075                | -32.90663          | -67.92207                 |
| $E_{\text{initial}}(e_1 \text{AOIHO})$ (eV)                   | -14.63489                                         | -14.63489               | -14.63489          | -14.53414                | -14.63489          | -14.63489                 |
| $E_{\text{initial}}(e_3 \text{AOIHO})$ (eV)                   | 0                                                 | -13.59844               | 0                  | -13.59844                | 0                  | -13.59844                 |
| $E_D(\text{Group})$ (eV)                                      | 5.63881                                           | 3.90454                 | 3.60401            | 7.43973                  | 3.63685            | 12.49186                  |

Table 15.247. The total bond energies of aniline and methyl-substituted anilines calculated using the functional group composition and the energies of Table 15.246 compared to the experimental values [2].

| Formula      | Name            | $\sum C=C$ | $\sum C-H$ (i) | $C-N$ (a)<br>Group | $NH_2$<br>Group | $C-C$ (a)<br>Group | $CH_3$ | Calculated<br>Total Bond Energy<br>(eV) | Experimental<br>Total Bond Energy<br>(eV) | Relative<br>Error |
|--------------|-----------------|------------|----------------|--------------------|-----------------|--------------------|--------|-----------------------------------------|-------------------------------------------|-------------------|
| $C_6H_5N$    | Aniline         | 6          | 5              | 1                  | 1               | 0                  | 0      | 64.4373                                 | 64.374                                    | -0.00093          |
| $C_7H_7N$    | 2-methylaniline | 6          | 4              | 1                  | 1               | 1                  | 1      | 76.62345                                | 76.643                                    | -0.00025          |
| $C_8H_9N$    | 3-methylaniline | 6          | 4              | 1                  | 1               | 1                  | 1      | 76.62345                                | 76.661                                    | 0.00050           |
| $C_9H_{11}N$ | 4-methylaniline | 6          | 4              | 1                  | 1               | 1                  | 1      | 76.62345                                | 76.654                                    | 0.00040           |

Table 15.248. The bond angle parameters of aniline and methyl-substituted anilines and experimental values [1].  $E_T$  is  $E_T(atom - atom, nsp^2, AO)$ .

| Atoms of Angle                 | $2c'$<br>Bond 1<br>( $a_n$ ) | $2c'$<br>Bond 2<br>( $a_n$ ) | $2c'$<br>Terminal<br>Atoms<br>( $a_n$ ) | $E_{\text{residual}}$<br>Atom 1 | Atom 1<br>Hybridization<br>Designation<br>(Table 15.3.A) | $E_{\text{residual}}$<br>Atom 2 | Atom 2<br>Hybridization<br>Designation<br>(Table 15.3.A) | $c_2$<br>Atom 1         | $c_2$<br>Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c'_2$  | $E_T$<br>(eV) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | $\theta_3$<br>( $^\circ$ ) | Cal. $\theta$<br>( $^\circ$ ) | Exp. $\theta$<br>( $^\circ$ ) |
|--------------------------------|------------------------------|------------------------------|-----------------------------------------|---------------------------------|----------------------------------------------------------|---------------------------------|----------------------------------------------------------|-------------------------|-----------------|-------|-------|-------|---------|---------------|----------------------------|----------------------------|----------------------------|-------------------------------|-------------------------------|
| $\angle(C' C'')$<br>(aromatic) | 2.62936                      | 2.62936                      | 4.5585                                  | -17.17218                       | 34                                                       | -17.17218                       | 34                                                       | 0.79232                 | 0.79232         | 1     | 1     | 1     | 0.79232 | -1.85536      |                            |                            |                            | 120.19                        | 120 [50-52]<br>(benzene)      |
| $\angle(C' H)$<br>(aromatic)   |                              |                              |                                         |                                 |                                                          |                                 |                                                          |                         |                 |       |       |       |         |               |                            |                            | 120.19                     | 120 [50-52]<br>(benzene)      |                               |
| $\angle HNH$                   | 1.88268                      | 1.88268                      | 3.1559                                  | -14.53414                       | N                                                        | H                               | H                                                        | 0.93613<br>Eq. (13.248) | 0.84665         | 1     | 1     | 0.75  | 1.06823 | 0             |                            |                            |                            | 113.89                        | 113.9<br>(aniline)            |
| $\angle HNC$                   | 1.88268                      | 2.69190                      | 4.0332                                  | -14.53414                       | N                                                        |                                 | 9                                                        | 0.86284<br>Eq. (15.152) | 0.75            | 0.75  | 1     | 0.75  | 1.01912 | 0             |                            |                            |                            | 122.70                        |                               |

## ARYL NITRO COMPOUNDS

Aryl nitro compounds have a hydrogen of an aryl group replaced by a nitro corresponding to an  $NO_2$  functional group and a  $C-N$  functional group. Examples include nitrobenzene, nitrophenol, and nitroaniline with formulas  $C_6H_5NO_2$ ,  $C_6H_5NO_3$ , and  $C_6H_6N_2O_2$ , respectively. The aromatic  $C \equiv C$  and  $C-H$  functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The  $OH$  and  $C-O$  functional groups of nitrophenols are the same as those of phenol given in the corresponding section. The  $NH_2$  and  $C-N$  functional groups of nitroanilines are the same as those of aniline given in the corresponding section. The differences between the total bond energies of the nitroanilines given in Table 15.252 are due to differences in the  $E_{osc}$  term. For simplicity and since the differences are small, the  $E_{osc}$  terms for nitroanilines were taken as the same.

The  $NO_2$  group is the same as that given in the Nitroalkanes section. The bond between the nitro and aromatic ring comprises a  $C-N$  functional group that is the same as that of nitroalkanes given in the corresponding section except that  $E_T(atom-atom,msp^3.AO)$  is  $-0.72457 eV$ , one half of that of the  $C-N$ -bond MO of nitroalkanes and equivalent to that of methyl (Eq. (14.151)) in order to maintain the independence and aromaticity of the benzene functional group. In addition, the energy terms due to oscillation in the transition state correspond to those of an aryl nitro compound.

The symbols of the functional groups of aryl nitro compounds are given in Table 15.249. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aryl nitro compounds are given in Tables 15.250, 15.251, and 15.252, respectively. The total energy of each aryl nitro compound given in Table 15.253 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.252 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_D(Group)$  ( $eV$ ) values based on composition is given by Eq. (15.58). The bond angle parameters of aryl nitro compounds determined using Eqs. (15.79-15.108) are given in Table 15.254.

Table 15.249. The symbols of functional groups of aryl nitro compounds.

| Functional Group      | Group Symbol    |
|-----------------------|-----------------|
| CC (aromatic bond)    | $^{3c}C=C$      |
| CH (aromatic)         | CH (i)          |
| Aryl C-N (aniline)    | C-N (a)         |
| Aryl C-N (nitro)      | C-N (b)         |
| Aryl C-O              | C-O (a)         |
| NO <sub>2</sub> group | NO <sub>2</sub> |
| NH <sub>2</sub> group | NH <sub>2</sub> |
| OH group              | OH              |

Table 15.250. The geometrical bond parameters of aryl nitro compounds and experimental values [1].

| Parameter                             | $^{3c}C=C$<br>Group    | CH (i)<br>Group   | C-N (a)<br>Group   | C-N (b)<br>Group | C-O (a)<br>Group  | NO <sub>2</sub><br>Group | NH <sub>2</sub><br>Group | OH<br>Group       |
|---------------------------------------|------------------------|-------------------|--------------------|------------------|-------------------|--------------------------|--------------------------|-------------------|
| $a$ ( $a_0$ )                         | 1.47348                | 1.60061           | 1.81158            | 1.97794          | 1.68220           | 1.33221                  | 1.24428                  | 1.26430           |
| $c'$ ( $a_0$ )                        | 1.31468                | 1.03299           | 1.34595            | 1.40639          | 1.29700           | 1.15421                  | 0.94134                  | 0.91808           |
| Bond Length<br>$2c'$ ( $\text{\AA}$ ) | 1.39140                | 1.09327           | 1.42449            | 1.48846          | 1.37268           | 1.22157                  | 0.99627                  | 0.971651          |
| Exp. Bond Length<br>( $\text{\AA}$ )  | 1.397 avg.<br>(phenol) | 1.084<br>(phenol) | 1.431<br>(aniline) |                  | 1.364<br>(phenol) | 1.224<br>(nitromethane)  | 0.998<br>(aniline)       | 0.956<br>(phenol) |
| $b, c$ ( $a_0$ )                      | 0.66540                | 1.22265           | 1.21254            | 1.39079          | 1.07126           | 0.66526                  | 0.81370                  | 0.86925           |
| $e$                                   | 0.89223                | 0.64537           | 0.74297            | 0.71104          | 0.77101           | 0.86639                  | 0.75653                  | 0.72615           |



Table 15.252. The energy parameters (eV) of functional groups of aryl nitro compounds.

| Parameters                                      | $\overset{3*}{C=C}$<br>Group | CH (I)<br>Group         | C-N (a)<br>Group | C-N (b)<br>Group | C-O (a)<br>Group | NO <sub>2</sub><br>Group | NH <sub>2</sub><br>Group | OH<br>Group        |
|-------------------------------------------------|------------------------------|-------------------------|------------------|------------------|------------------|--------------------------|--------------------------|--------------------|
| $f_1$                                           | 0.75                         | 1                       |                  |                  |                  |                          |                          |                    |
| $n_1$                                           | 2                            | 1                       | 1                | 1                | 1                | 2                        | 2                        | 1                  |
| $n_2$                                           | 0                            | 0                       | 0                | 0                | 0                | 0                        | 0                        | 0                  |
| $n_3$                                           | 0                            | 0                       | 0                | 0                | 0                | 0                        | 1                        | 0                  |
| $C_1$                                           | 0.5                          | 0.75                    | 0.5              | 0.5              | 0.5              | 0.5                      | 0.75                     | 0.75               |
| $C_2$                                           | 0.85252                      | 1                       | 1                | 1                | 1                | 1                        | 0.93613                  | 1                  |
| $c_1$                                           | 1                            | 1                       | 1                | 1                | 1                | 1                        | 0.75                     | 0.75               |
| $c_2$                                           | 0.85252                      | 0.91771                 | 0.84665          | 0.91140          | 0.79329          | 0.85987                  | 0.92171                  | 1                  |
| $c_3$                                           | 0                            | 1                       | 0                | 0                | 0                | 0                        | 0                        | 1                  |
| $c_4$                                           | 3                            | 1                       | 2                | 2                | 2                | 4                        | 1                        | 1                  |
| $c_5$                                           | 0                            | 1                       | 0                | 0                | 0                | 0                        | 2                        | 1                  |
| $C_{10}$                                        | 0.5                          | 0.75                    | 0.5              | 0.5              | 0.5              | 0.5                      | 1.5                      | 0.75               |
| $C_{20}$                                        | 0.85252                      | 1                       | 1                | 1                | 1                | 1                        | 1                        | 1                  |
| $V_e$ (eV)                                      | -101.12679                   | -37.10024               | -32.76465        | -31.36351        | -34.04658        | -106.90919               | -78.97795                | -40.92709          |
| $V_p$ (eV)                                      | 20.69825                     | 13.17125                | 10.10870         | 9.67426          | 10.49024         | 23.57588                 | 28.90735                 | 14.81988           |
| $T$ (eV)                                        | 34.31559                     | 11.58941                | 9.04312          | 7.92833          | 10.11966         | 40.12475                 | 31.73641                 | 16.18567           |
| $V_m$ (eV)                                      | -17.15779                    | -5.79470                | -4.52156         | -3.96416         | -5.05983         | -20.06238                | -15.86820                | -8.09284           |
| $E(\lambda_{OH})$ (eV)                          | 0                            | -14.63489               | -14.63489        | -14.63489        | -14.63489        | 0                        | -14.53414                | -13.6181           |
| $\Delta E_{H_2\lambda_{OH}}(\lambda_{OH})$ (eV) | 0                            | -1.13379                | -1.13379         | -0.72457         | -1.49608         | 0                        | 0                        | 0                  |
| $E_T(\lambda_{OH})$ (eV)                        | 0                            | -13.50110               | -13.50110        | -13.91032        | -13.13881        | 0                        | -14.53414                | -13.6181           |
| $E(n, \lambda_{OH})$ (eV)                       | 0                            | 0                       | 0                | 0                | 0                | 0                        | -14.53414                | 0                  |
| $E_T(H_2\lambda_{OH})$ (eV)                     | -63.27075                    | -31.63539               | -31.63549        | -31.63540        | -31.63532        | -63.27093                | -48.73654                | -31.63247          |
| $E_T(atom-atom, msp^3.AO)$ (eV)                 | -2.26759                     | -0.56690                | -1.13379         | -0.72457         | -1.49608         | -3.71673                 | 0                        | 0                  |
| $E_T(\lambda_{OH})$ (eV)                        | -65.53833                    | -32.20226               | -32.76916        | -32.35994        | -33.13145        | -66.98746                | -48.73660                | -31.63537          |
| $\omega$ (10 <sup>15</sup> rad / s)             | 49.7272                      | 26.4826                 | 11.9890          | 17.8228          | 13.3984          | 19.0113                  | 68.9812                  | 44.1776            |
| $E_K$ (eV)                                      | 32.73133                     | 17.43132                | 7.89138          | 11.73128         | 8.81907          | 12.51354                 | 45.40465                 | 29.07844           |
| $\bar{E}_D$ (eV)                                | -0.35806                     | -0.26130                | -0.18211         | -0.21927         | -0.19465         | -0.23440                 | -0.42172                 | -0.33749           |
| $\bar{E}_{K_{orb}}$ (eV)                        | 0.19649<br>[49]              | 0.35532<br>Eq. (13.458) | 0.15498<br>[54]  | 0.10539<br>[45]  | 0.12808<br>[19]  | 0.19342<br>[45]          | 0.40929<br>[22]          | 0.46311<br>[17-18] |
| $\bar{E}_{enc}$ (eV)                            | -0.25982                     | -0.08364                | -0.10462         | -0.16658         | -0.13061         | -0.13769                 | -0.21708                 | -0.10594           |
| $E_{mng}$ (eV)                                  | 0.14803                      | 0.14803                 | 0.14803          | 0.14803          | 0.14803          | 0.11441                  | 0.14803                  | 0.11441            |
| $E_T(Grp)$ (eV)                                 | -49.54347                    | -32.28590               | -32.87379        | -32.52652        | -33.26206        | -67.26284                | -49.17075                | -31.74130          |
| $E_{initial}(c, \lambda_{OH})$ (eV)             | -14.63489                    | -14.63489               | -14.63489        | -14.63489        | -14.63489        | -14.63489                | -14.53414                | -13.6181           |
| $E_{initial}(c, \lambda_{OH})$ (eV)             | 0                            | -13.59844               | 0                | 0                | 0                | 0                        | -13.59844                | -13.59844          |
| $E_D(Grp)$ (eV)                                 | 5.63881                      | 3.90454                 | 3.60401          | 3.25674          | 3.99228          | 8.72329                  | 7.43973                  | 4.41035            |



Table 15.253. The total bond energies of aryl nitro compounds calculated using the functional group composition and the energies of Table 15.252 compared to the experimental values [2]. The magnetic energy  $E_{mag}$  that is subtracted from the weighed sum of the  $E_D$  ( $group$ ) ( $e$ ) values based on composition is given by (15.58).

| Formula          | Name              | $C \equiv C$ | $CH$ (i) | $C-N$ (a) | $C-N$ (b) | $C-O$ (a) | $NO_2$ | $NH_2$ | $OH$ | $E_{mag}$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|------------------|-------------------|--------------|----------|-----------|-----------|-----------|--------|--------|------|-----------|-----------------------------------|-------------------------------------|----------------|
| $C_6H_5NO_2$     | Nitrobenzene      | 6            | 5        | 0         | 1         | 0         | 1      | 0      | 0    | 1         | 65.18754                          | 65.217                              | 0.00046        |
| $C_6H_4(NO_2)_2$ | 2,4-dinitrophenol | 6            | 4        | 0         | 2         | 1         | 2      | 1      | 0    | 2         | 71.61308                          | 71.642                              | 0.00037        |
| $C_6H_5NO_2$     | 2-nitroaniline    | 6            | 4        | 1         | 1         | 0         | 1      | 1      | 0    | 0         | 72.47476                          | 72.424                              | -0.00050       |
| $C_6H_4(NO_2)_2$ | 3-nitroaniline    | 6            | 4        | 1         | 1         | 0         | 1      | 1      | 0    | 0         | 72.47476                          | 72.481                              | -0.00009       |
| $C_6H_3(NO_2)_3$ | 4-nitroaniline    | 6            | 4        | 1         | 1         | 0         | 1      | 1      | 0    | 0         | 72.47476                          | 72.476                              | -0.00002       |

Table 15.254. The bond angle parameters of aryl nitro compounds and experimental values [1].  $E_T$  is  $E_T(atom - atom, mp^3 AO)$ .

| Atom of Angle           | $2c'$ Bond 1 ( $a_1$ ) | $2c'$ Bond 2 ( $a_2$ ) | $2c'$ Terminal Atom ( $a_3$ ) | $E_{Terminal}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3.A) | $E_{Terminal}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | $c_2$ Atom 1               | $c_2$ Atom 2               | $C_1$ | $C_2$ | $\varphi_1$ | $\varphi_2$ | $E_T$ (eV) | $\theta_r$ ( $^\circ$ ) | $\theta_l$ ( $^\circ$ ) | $\theta_2$ ( $^\circ$ ) | Cal. $\theta$ ( $^\circ$ ) | Exp. $\theta$ ( $^\circ$ ) |
|-------------------------|------------------------|------------------------|-------------------------------|-----------------------|-------------------------------------------------|-----------------------|-------------------------------------------------|----------------------------|----------------------------|-------|-------|-------------|-------------|------------|-------------------------|-------------------------|-------------------------|----------------------------|----------------------------|
| $\angle CCC$ (aromatic) | 2.6936                 | 2.6936                 | 4.585                         | -17.17218             | 34                                              | -17.17218             | 34                                              | 0.79332                    | 0.79332                    | 1     | 1     | 1           |             | -1.85836   |                         |                         |                         | 120.19                     | 120 [50-52] (benzene)      |
| $\angle CCH$ (aromatic) |                        |                        |                               |                       |                                                 |                       |                                                 |                            |                            |       |       |             |             |            |                         | 120.19                  |                         | 120 [50-52] (benzene)      |                            |
| $\angle ONO$            | 2.30843                | 2.30843                | 4.1231                        | -16.68411             | 24                                              | -16.68411             | 24                                              | 0.81549                    | 0.81549                    | 1     | 1     | 1           |             | -1.44915   |                         |                         |                         | 126.52                     | 123.2 [54] (nitrobenzene)  |
| $\angle CNO$            | 2.81279                | 2.30843                | 4.4159                        | -17.45562             | 40                                              | -13.61806             | 0                                               | 0.77945                    | 0.85595 ( $E_T$ ) (15.114) | 1     | 1     | 1           |             | -1.65376   |                         |                         |                         | 118.5 [54] (nitrobenzene)  | 125.3 (nitrobenzene)       |
| $\angle C'OH$           | 2.59399                | 1.83616                | 3.6515                        | -14.82575             | 1                                               | -14.82575             | 1                                               | 0.91771                    | 0.91771                    | 0.75  | 1     | 0.75        |             | 0          |                         |                         |                         | 109.84                     | 109.0 (phenol)             |
| $\angle HNH$            | 1.88268                | 1.88268                | 3.1559                        | -14.53414             | N                                               | H                     | H                                               | 0.84665 ( $E_T$ ) (13.248) | 0.84665 ( $E_T$ ) (13.248) | 1     | 1     | 1           |             | 0          |                         |                         |                         | 113.9                      | 113.9 (aniline)            |
| $\angle C'NH$           | 2.69190                | 1.88268                | 3.9833                        | -15.95955             | 9                                               | -14.53414             | N                                               | 0.84665 ( $E_T$ ) (15.152) | 0.84665 ( $E_T$ ) (15.152) | 0.75  | 1     | 0.75        |             | 0          |                         |                         |                         | 120.05                     |                            |

## BENZOIC ACID COMPOUNDS

Benzoic acid compounds have a hydrogen of an aryl group replaced by a carboxylic acid group corresponding to an  $C-C(O)-OH$  moiety that comprises  $C=O$  and  $OH$  functional groups that are the same as those of carboxylic acids given in the corresponding 5 section. The single bond of aryl carbon to the carbonyl carbon atom,  $C-C(O)$ , is also a functional group. This group is also equivalent to the same group of carboxylic acids except that  $\Delta E_{H_2MO}(AO/HO)$  in Eq. (15.42) and  $E_r(atom-atom,msp^3.AO)$  in Eq. (15.52) are both  $-1.29147\text{ eV}$  which is a linear combination of  $\frac{-1.13379\text{ eV}}{2}$ ,  $E_r(atom-atom,msp^3.AO)$  of the  $C-H$  group that the  $C-C(O)$  group replaces, and that 10 of an independent  $C2sp^3\text{ HO}$ ,  $-0.72457\text{ eV}$  (Eq. (14.151)).

Examples include benzoic acid, chlorobenzoic acid, and aniline carboxylic acid with formulas  $C_7H_6O_2$ ,  $C_7H_5O_2Cl$ , and  $C_7H_7NO_2$ , respectively. The aromatic  $C\equiv C$  and  $C-H$  functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic 15 Compounds section. The  $NH_2$  and  $C-N$  functional groups of aniline carboxylic acids are the same as those of aniline given in the corresponding section. The  $C-Cl$  functional group of 2-chlorobenzoic acids corresponding to meta substitution is equivalent to that of chlorobenzene given in the corresponding section. The  $C-Cl$  functional group of 3 or 4-chlorobenzoic acids corresponding to ortho and para substitution is also equivalent to that of 20 chlorobenzene, except that  $\Delta E_{H_2MO}(AO/HO)$  in Eq. (15.42) and  $E_r(atom-atom,msp^3.AO)$  in Eq. (15.52) are both  $-0.92918\text{ eV}$  (Eq. (14.513)) since each of these positions can form a resonance structure with the carboxylic acid group which is permissive of greater charge donation from the  $C2sp^3\text{ HO}$ .

The symbols of the functional groups of benzoic acid compounds are given in Table 25 15.255. The corresponding designations of benzoic acid is shown in Figure 64. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of benzoic acid compounds are given in Tables 15.256, 15.257, and 15.258, respectively. The total energy of each benzoic acid compound given in Table 15.259 was calculated as the sum over the integer multiple of

each  $E_D(\text{Group})$  of Table 15.258 corresponding to functional-group composition of the molecule. The bond angle parameters of benzoic acid compounds determined using Eqs. (15.79-15.108) are given in Table 15.260.

5 Table 15.255. The symbols of functional groups of benzoic acid compounds.

| Functional Group                                          | Group Symbol          |
|-----------------------------------------------------------|-----------------------|
| CC (aromatic bond)                                        | $\overset{3e}{C} = C$ |
| CH (aromatic)                                             | CH (i)                |
| C-C(O)                                                    | C - C(O)              |
| C=O (aryl carboxylic acid)                                | C = O                 |
| (O)C-O                                                    | C - O                 |
| OH group                                                  | OH                    |
| Cl - C (Cl to aromatic bond of 2-chlorobenzoic acid)      | C - Cl (i)            |
| Cl - C (Cl to aromatic bond of 3 or 4-chlorobenzoic acid) | C - Cl (ii)           |
| Aryl C-N (aniline)                                        | C - N                 |
| NH <sub>2</sub> group                                     | NH <sub>2</sub>       |

Table 15.256. The geometrical bond parameters of benzoic acid compounds and experimental values [1].

| Parameter                  | C=C<br>Group       | CH (i)<br>Group    | C-C(O)<br>Group             | C=O<br>Group           | C-O<br>Group              | OH<br>Group            | C-Cl (i)<br>Group        | C-Cl (ii)<br>Group       | C-N<br>Group       | NH <sub>2</sub><br>Group |
|----------------------------|--------------------|--------------------|-----------------------------|------------------------|---------------------------|------------------------|--------------------------|--------------------------|--------------------|--------------------------|
| $a$ (Å)                    | 1.47348            | 1.60061            | 1.93111                     | 1.29907                | 1.73490                   | 1.26430                | 2.20799                  | 2.19358                  | 1.81158            | 1.24428                  |
| $c'$ (Å)                   | 1.31468            | 1.03299            | 1.39682                     | 1.13977                | 1.31716                   | 0.91808                | 1.64782                  | 1.64243                  | 1.34595            | 0.94134                  |
| Bond Length<br>2c' (Å)     | 1.39140            | 1.09327            | 1.47833                     | 1.20628                | 1.39402                   | 0.971651               | 1.74397                  | 1.73827                  | 1.42449            | 0.99627                  |
| Exp. Bond<br>Length<br>(Å) | 1.399<br>(benzene) | 1.101<br>(benzene) | 1.48 [55]<br>(benzoic acid) | 1.214<br>(acetic acid) | 1.393<br>(methyl formate) | 0.972<br>(formic acid) | 1.737<br>(chlorobenzene) | 1.737<br>(chlorobenzene) | 1.431<br>(aniline) | 0.998<br>(aniline)       |
| $h_c$ (Å)                  | 0.66540            | 1.22265            | 1.36225                     | 0.62331                | 1.12915                   | 0.86925                | 1.46967                  | 1.45403                  | 1.21254            | 0.81370                  |
| $e$                        | 0.89223            | 0.64537            | 0.71591                     | 0.87737                | 0.75921                   | 0.72615                | 0.74630                  | 0.74874                  | 0.74297            | 0.75653                  |

Table 15.257. The MO to HO intercept geometrical bond parameters of benzoic acid compounds.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{msp}^2 \text{AO})$ .

| Bond                                                             | Atom  | $E_T$<br>(eV)<br>Bond 1 | $E_T$<br>(eV)<br>Bond 2 | $E_T$<br>(eV)<br>Bond 3 | $E_T$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>( $2sp^2$ )<br>(eV) | $r_{\text{final}}$<br>( $a_0$ ) | $r_{\text{final}}$<br>( $a_0$ )<br>Final | $E_{\text{total}}(\text{Casp})$<br>(eV)<br>Final | $E(2sp^2)$<br>(eV)<br>Final | $\theta'$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | $d_1$<br>( $a_0$ ) | $d_2$<br>( $a_0$ ) |
|------------------------------------------------------------------|-------|-------------------------|-------------------------|-------------------------|-------------------------|----------------------------------------------|---------------------------------|------------------------------------------|--------------------------------------------------|-----------------------------|---------------------------|----------------------------|----------------------------|--------------------|--------------------|
| $C^* - H$ ( $C^*H$ )                                             | $C^*$ | -0.85035                | -0.85035                | -0.56690                | 0                       | -153.88327                                   | 0.91771                         | 0.79597                                  | -17.09334                                        | -16.90248                   | 74.42                     | 105.58                     | 38.84                      | 1.24678            | 0.21379            |
| $C^* = HC^* = C^*$                                               | $C^*$ |                         |                         |                         |                         |                                              |                                 |                                          |                                                  |                             |                           |                            |                            |                    |                    |
| $C^* = (HCOX^*)C^* = C^*(H)_e$                                   | $C^*$ |                         |                         |                         | 0                       | -153.88327                                   | 0.91771                         | 0.79597                                  | -17.09334                                        | -16.90248                   | 134.24                    | 45.76                      | 58.98                      | 0.79595            | 0.55533            |
| $C^* = (C^*)C^* = C^*(H)$                                        | $C^*$ |                         |                         |                         |                         |                                              |                                 |                                          |                                                  |                             |                           |                            |                            |                    |                    |
| $C^* = (H_2N)C^* = C^*(H)$                                       | $C^*$ |                         |                         |                         |                         |                                              |                                 |                                          |                                                  |                             |                           |                            |                            |                    |                    |
| $(C^*) = C^*(O)O - H$                                            | O     | -0.92918                | 0                       | 0                       | 0                       |                                              | 1.00000                         | 0.86359                                  | -15.75403                                        |                             | 115.09                    | 64.91                      | 64.12                      | 0.55182            | 0.36025            |
| $(C^*) = C^*(O) - OH$                                            | O     | -0.92918                | 0                       | 0                       | 0                       |                                              | 1.00000                         | 0.86359                                  | -15.75403                                        |                             | 101.32                    | 78.68                      | 48.58                      | 1.14765            | 0.16930            |
| $(C^*) = C^*(O) - OH$                                            | $C^*$ | -0.92918                | -1.34946                | -0.64574                | 0                       | -154.54007                                   | 0.91771                         | 0.76652                                  | -17.75013                                        | -17.55927                   | 93.11                     | 86.89                      | 42.68                      | 1.27551            | 0.04165            |
| $(C^*) = C^*(OH) = O$                                            | O     | -1.34946                | 0                       | 0                       | 0                       |                                              | 1.00000                         | 0.84115                                  | -16.17521                                        |                             | 137.27                    | 42.73                      | 66.31                      | 0.52193            | 0.61784            |
| $(C^*) = C^*(OH) = O$                                            | $C^*$ | -1.34946                | -0.64574                | -0.92918                | 0                       | -154.54007                                   | 0.91771                         | 0.76652                                  | -17.75013                                        | -17.55927                   | 134.03                    | 45.97                      | 62.14                      | 0.60699            | 0.53278            |
| $C^* = (HCOX^*)C^* = C^*$<br>( $C^*$ bound to H, Cl, or $NH_2$ ) | $C^*$ | -0.64574                | -0.83035                | -0.83035                | 0                       | -153.96212                                   | 0.91771                         | 0.79232                                  | -17.17218                                        | -16.98132                   | 134.09                    | 45.91                      | 58.79                      | 0.76344            | 0.55124            |
| $(C^*) = (C^* - Cl)$                                             | Cl    | -0.36229                | 0                       | 0                       | 0                       |                                              | 1.05158                         | 0.89582                                  | 15.18804                                         |                             | 82.92                     | 97.08                      | 37.22                      | 1.75824            | 0.11042            |
| $(C^*) = (C^* - Cl)$                                             | $C^*$ | -0.36229                | -0.83035                | -0.83035                | 0                       | -153.67867                                   | 0.91771                         | 0.80561                                  | -16.88873                                        | -16.69786                   | 73.32                     | 106.68                     | 31.67                      | 1.87911            | 0.23129            |
| $C^* = (C^*)C^* = C^*$<br>( $C^*$ bound to H or Cl)              | $C^*$ | -0.36229                | -0.83035                | -0.83035                | 0                       | -153.67867                                   | 0.91771                         | 0.80561                                  | -16.88873                                        | -16.69786                   | 134.65                    | 45.35                      | 50.47                      | 0.74854            | 0.56614            |
| $(C^*) = C^*NH - H$                                              | N     | -0.56690                | 0                       | 0                       | 0                       |                                              | 0.95084                         | 0.88392                                  | -15.39265                                        |                             | 121.74                    | 58.26                      | 67.49                      | 0.47634            | 0.46500            |
| $(C^*) = C^* - NH_2$                                             | $C^*$ | -0.56690                | -0.83035                | -0.83035                | 0                       | -153.88328                                   | 0.91771                         | 0.79597                                  | -17.09334                                        | -16.90248                   | 88.49                     | 91.51                      | 41.01                      | 1.36696            | 0.02101            |
| $(C^*) = C^* - NH_2$                                             | N     | -0.56690                | 0                       | 0                       | 0                       |                                              | 0.95084                         | 0.88392                                  | -15.39265                                        |                             | 96.32                     | 83.68                      | 46.43                      | 1.24859            | 0.09736            |
| $C^* = (H_2N)C^* = C^*$                                          | $C^*$ | -0.85035                | -0.85035                | -0.56690                | 0                       | -153.88327                                   | 0.91771                         | 0.79597                                  | -17.09334                                        | -16.90248                   | 134.24                    | 45.76                      | 58.98                      | 0.75935            | 0.55533            |

Table 15.238. The energy parameters (eV) of functional groups of benzoic acid compounds.

| Parameters                        | C=C<br>Group | C-H (i)<br>Group        | C-C(O)<br>Group | C=O<br>Group | C-O<br>Group | OH<br>Group | C-Cl (i)<br>Group | C-Cl (ii)<br>Group | C-N<br>Group | NH <sub>2</sub><br>Group |
|-----------------------------------|--------------|-------------------------|-----------------|--------------|--------------|-------------|-------------------|--------------------|--------------|--------------------------|
| $I_1$                             | 0.75         | 1                       |                 |              |              |             |                   |                    |              |                          |
| $n_1$                             | 2            | 1                       | 1               | 2            | 1            | 1           | 1                 | 1                  | 1            | 2                        |
| $n_2$                             | 0            | 0                       | 0               | 0            | 0            | 0           | 0                 | 0                  | 0            | 0                        |
| $n_3$                             | 0            | 0                       | 0               | 0            | 0            | 0           | 0                 | 0                  | 0            | 1                        |
| $c_1$                             | 0.5          | 0.75                    | 0.5             | 0.5          | 0.5          | 0.75        | 0.5               | 0.5                | 0.5          | 0.75                     |
| $c_2$                             | 0.85252      | 1                       | 1               | 1            | 1            | 1           | 0.81317           | 0.81317            | 1            | 0.95613                  |
| $c_3$                             | 1            | 1                       | 1               | 1            | 1            | 0.75        | 1                 | 1                  | 1            | 0.75                     |
| $c_4$                             | 0.85252      | 0.91771                 | 0.91771         | 0.85395      | 0.85395      | 1           | 1                 | 1                  | 0.84665      | 0.92171                  |
| $c_5$                             | 0            | 1                       | 0               | 2            | 0            | 1           | 0                 | 0                  | 0            | 0                        |
| $c_6$                             | 3            | 1                       | 2               | 4            | 2            | 1           | 2                 | 2                  | 2            | 1                        |
| $c_7$                             | 0            | 1                       | 0               | 0            | 0            | 1           | 0                 | 0                  | 0            | 2                        |
| $c_8$                             | 0.5          | 0.75                    | 0.5             | 0.5          | 0.5          | 0.75        | 0.5               | 0.5                | 0.5          | 1.5                      |
| $c_9$                             | 0.85252      | 1                       | 1               | 1            | 1            | 1           | 0.81317           | 0.81317            | 1            | 1                        |
| $c_{10}$                          | -101.12679   | -37.10024               | -32.15216       | -111.25473   | -35.08488    | -40.92709   | -31.85648         | -32.14474          | -32.76465    | -78.97795                |
| $V_1$ (eV)                        | 20.69825     | 13.17125                | 9.74055         | 23.87467     | 10.32968     | 14.81988    | 8.2686            | 8.28394            | 10.10870     | 28.90735                 |
| $V_2$ (eV)                        | 34.31559     | 11.58941                | 8.23945         | 42.82081     | 10.11150     | 16.18567    | 7.21391           | 7.32700            | 9.04312      | 31.73641                 |
| $V_3$ (eV)                        | -17.15779    | -5.79470                | -4.11973        | -21.41040    | -5.0575      | -8.09284    | -3.60695          | -3.66350           | -4.52156     | -15.86820                |
| $E_1$ (eV)                        | 0            | -14.63489               | -14.63489       | 0            | -14.63489    | -13.6181    | -14.63489         | -14.63489          | -14.63489    | -14.53414                |
| $\Delta E_{1/2}$ (eV)             | 0            | -1.13379                | -1.29147        | -2.69893     | -2.69893     | 0           | -2.99216          | -2.99216           | -1.13379     | 0                        |
| $E_{1/2}$ (eV)                    | 0            | -13.50110               | -13.34342       | 2.69893      | -11.93596    | -13.6181    | -11.64273         | -11.64273          | -13.50110    | -14.53414                |
| $E_{1/2}$ (eV)                    | 0            | 0                       | 0               | 0            | 0            | 0           | 0                 | 0                  | 0            | -14.53414                |
| $E_{1/2}$ (eV)                    | -63.27075    | -31.63539               | -31.63530       | -63.27074    | -31.63541    | -31.63247   | -31.63539         | -31.63542          | -31.63549    | -48.73654                |
| $E_{1/2}$ (eV)                    | -2.26759     | -0.56690                | -1.29147        | -2.69893     | -1.85836     | 0           | -0.72457          | -0.92918           | -1.13379     | 0                        |
| $E_{1/2}$ (eV)                    | -65.53833    | -32.70226               | -32.92684       | -65.96966    | -33.49373    | -31.63537   | -32.35994         | -32.56455          | -32.76916    | -48.73660                |
| $\omega$ (10 <sup>15</sup> rad/s) | 49.7272      | 26.4826                 | 10.7262         | 59.4034      | 24.3637      | 44.1776     | 8.03459           | 8.11389            | 11.9890      | 68.9812                  |
| $E_g$ (eV)                        | 32.73133     | 17.43132                | 7.06019         | 39.10034     | 16.03660     | 29.07844    | 5.28851           | 5.34070            | 7.89138      | 45.40465                 |
| $E_g$ (eV)                        | -0.35806     | -0.26130                | -0.17309        | -0.40804     | -0.26535     | -0.33749    | -0.14722          | -0.14888           | -0.18211     | -0.42172                 |
| $E_{gap}$ (eV)                    | 0.19649      | 0.35532                 | 0.10502         | 0.21077      | 0.14010      | 0.46311     | 0.08059           | 0.08059            | 0.15498      | 0.40929                  |
| $E_{gap}$ (eV)                    | [49]         | E <sub>g</sub> (13.458) | [29]            | [12]         | [31]         | [17-18]     | [12]              | [12]               | [54]         | [22]                     |
| $E_{gap}$ (eV)                    | -0.25982     | -0.08364                | -0.12058        | -0.30266     | -0.19530     | -0.10594    | -0.10693          | -0.10839           | -0.10462     | -0.21708                 |
| $E_{gap}$ (eV)                    | 0.14803      | 0.14803                 | 0.14803         | 0.11441      | 0.14803      | 0.11441     | 0.14803           | 0.14803            | 0.14803      | 0.14803                  |
| $E_{1/2}$ (eV)                    | -49.54347    | -32.28590               | -33.04742       | -66.57498    | -33.68903    | -31.74130   | -32.46687         | -32.67314          | -32.87379    | -49.17075                |
| $E_{1/2}$ (eV)                    | -14.63489    | -14.63489               | -14.63489       | -14.63489    | -14.63489    | -13.6181    | -14.63489         | -14.63489          | -14.63489    | -14.53414                |
| $E_{1/2}$ (eV)                    | 0            | -13.59844               | 0               | 0            | 0            | -13.59844   | 0                 | 0                  | 0            | -13.59844                |
| $E_{1/2}$ (eV)                    | 5.63881      | 3.90454                 | 3.77764         | 7.80660      | 4.41925      | 4.41035     | 3.19709           | 3.40356            | 3.60401      | 7.43973                  |

Table 15.259. The total bond energies of benzoic acid compounds calculated using the functional group composition and the energies of Table 15.258 compared to the experimental values [2].

| Formula                                                       | Name                      | C=C Group | C-H (i) Group | C-C(O) Group | C=O Group | C-O Group | O-H Group | C-Cl (i) Group | C-Cl (ii) Group | C-N Group | NH <sub>2</sub> Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|---------------------------------------------------------------|---------------------------|-----------|---------------|--------------|-----------|-----------|-----------|----------------|-----------------|-----------|-----------------------|-----------------------------------|-------------------------------------|----------------|
| C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub>                 | Benzoic acid              | 6         | 3             | 1            | 0         | 1         | 1         | 0              | 0               | 0         | 0                     | 73.6038                           | 73.762                              | -0.00009       |
| C <sub>6</sub> H <sub>4</sub> ClCO <sub>2</sub>               | 2-chlorobenzoic acid      | 6         | 4             | 1            | 0         | 1         | 1         | 1              | 0               | 0         | 0                     | 73.06193                          | 73.082                              | 0.00027        |
| C <sub>6</sub> H <sub>3</sub> Cl <sub>2</sub> CO <sub>2</sub> | 3-chlorobenzoic acid      | 6         | 4             | 1            | 0         | 1         | 1         | 0              | 0               | 0         | 0                     | 73.26820                          | 73.261                              | -0.00010       |
| C <sub>6</sub> H <sub>2</sub> Cl <sub>3</sub> CO <sub>2</sub> | 4-chlorobenzoic acid      | 6         | 4             | 1            | 0         | 1         | 1         | 0              | 0               | 0         | 0                     | 73.26820                          | 73.247                              | -0.00028       |
| C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>                 | Aniline-2-carboxylic acid | 6         | 4             | 1            | 1         | 1         | 1         | 0              | 0               | 1         | 1                     | 80.90857                          | 80.941                              | 0.00041        |
| C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>                 | Aniline-3-carboxylic acid | 6         | 4             | 1            | 1         | 1         | 1         | 0              | 0               | 1         | 1                     | 80.90857                          | 80.813                              | -0.00118       |
| C <sub>6</sub> H <sub>3</sub> NO <sub>2</sub>                 | Aniline-4-carboxylic acid | 6         | 4             | 1            | 1         | 1         | 1         | 0              | 0               | 1         | 1                     | 80.90857                          | 80.949                              | 0.00030        |

Table 15.260. The bond angle parameters of benzoic acid compounds and experimental values [1]. E<sub>r</sub> is E<sub>r</sub>(atom-atom, mp<sup>3</sup>, A.O.).

| Atoms of Angle  | 2c <sup>a</sup> Bond 1 (a <sub>0</sub> ) | 2c <sup>a</sup> Bond 2 (a <sub>0</sub> ) | 2c <sup>a</sup> Terminal Atoms (a <sub>0</sub> ) | E <sub>r</sub> (atom-atom, mp <sup>3</sup> , A.O.) | Atom 1 Hybridization Designation (Table 15.3.A) | F <sub>terminal</sub> Atom 2 | Atom 2 Hybridization Designation (Table 15.3.A) | S <sub>2</sub> Atom 1               | S <sub>2</sub> Atom 2               | C <sub>1</sub> | C <sub>2</sub> | γ <sub>1</sub> | γ <sub>2</sub> | E <sub>r</sub> (eV) | θ <sub>r</sub> (°) | θ <sub>1</sub> (°) | θ <sub>2</sub> (°) | Cal θ (°) | Exp. θ (°)                                                                  |
|-----------------|------------------------------------------|------------------------------------------|--------------------------------------------------|----------------------------------------------------|-------------------------------------------------|------------------------------|-------------------------------------------------|-------------------------------------|-------------------------------------|----------------|----------------|----------------|----------------|---------------------|--------------------|--------------------|--------------------|-----------|-----------------------------------------------------------------------------|
| ZC(C)(aromatic) | 2.62956                                  | 2.62956                                  | 4.5585                                           | -17.17218                                          | 34                                              | -17.17218                    | 34                                              | 0.79232                             | 0.79232                             | 1              | 1              | 1              | 0.79232        | -1.83836            |                    |                    |                    | 120.19    | 120 [50-52] (benzene)                                                       |
| ZC(C)(aromatic) |                                          |                                          |                                                  |                                                    |                                                 |                              |                                                 |                                     |                                     |                |                |                |                |                     |                    |                    |                    | 119.91    | 120 [50-52] (benzene)                                                       |
| ZC(C)(aromatic) | 2.63431                                  | 1.82616                                  | 3.6405                                           | -14.82575                                          | 1                                               | -14.82575                    | 1                                               | 1                                   | 0.91771                             | 0.75           | 1              | 0.75           | 0.91771        | 0                   |                    |                    |                    | 107.71    |                                                                             |
| ZC(C)(aromatic) | 2.82796                                  | 2.27954                                  | 4.4721                                           | -17.17218                                          | 34                                              | -17.17218                    | 34                                              | 0.79232                             | 0.83395 (E <sub>0</sub> ) (15.1143) | 1              | 1              | 1              | 0.82313        | -1.65376            |                    |                    |                    | 121.86    | 122 [55] (benzoic acid)                                                     |
| ZC(C)(aromatic) | 2.82796                                  | 2.63431                                  | 4.6690                                           | -16.40067                                          | 19                                              | -16.40067                    | 19                                              | 0.82959                             | 0.83395 (E <sub>0</sub> ) (15.1143) | 1              | 1              | 1              | 0.84177        | -1.65376            |                    |                    |                    | 117.43    | 118 [55] (benzoic acid)                                                     |
| ZC(C)(aromatic) | 2.37954                                  | 2.63431                                  | 4.3818                                           | -16.17521                                          | 12                                              | -16.17521                    | 12                                              | 0.84115                             | 0.86339                             | 1              | 1              | 1              | 0.85237        | -1.44915            |                    |                    |                    | 126.03    | 122 [55] (benzoic acid)                                                     |
| ZC(C)(aromatic) |                                          |                                          |                                                  |                                                    |                                                 |                              |                                                 |                                     |                                     |                |                |                |                |                     |                    |                    |                    |           | 120                                                                         |
| ZC(C)(aromatic) | 2.62956                                  | 2.62956                                  | 4.5585                                           | -17.17218                                          | 34                                              | -17.17218                    | 34                                              | 0.79232                             | 0.79232                             | 1              | 1              | 1              | 0.79232        | -1.83836            |                    |                    |                    | 120.19    | (ZCC(H)C chlorobenzene) 121.7 (ZCC(C)C chlorobenzene) 120 [50-52] (benzene) |
| ZC(C)(aromatic) |                                          |                                          |                                                  |                                                    |                                                 |                              |                                                 |                                     |                                     |                |                |                |                |                     |                    |                    |                    | 119.91    | 120 [50-52] (benzene)                                                       |
| ZHNH            | 1.88268                                  | 1.88268                                  | 3.1559                                           | -14.53414                                          | N                                               | -14.53414                    | N                                               | 0.95615 (E <sub>0</sub> ) (13.2480) | 0.84665 (E <sub>0</sub> ) (15.1523) | 1              | 1              | 0.75           | 1.06823        | 0                   |                    |                    |                    | 113.89    | 113.9 (aniline)                                                             |
| ZC(NH)          | 2.69190                                  | 1.88268                                  | 3.9855                                           | -15.95955                                          | 9                                               | -15.95955                    | 9                                               |                                     |                                     | 0.75           | 1              | 0.75           | 1.08900        | 0                   |                    |                    |                    | 120.05    |                                                                             |

## ANISOLE

Anisole has the formula  $C_7H_8O$  and comprises the phenol molecule with the hydroxyl hydrogen atom replaced by the moiety  $-O-CH_3$  to form an ether comprising aromatic and methyl functional groups as well as two types of  $C-O$  functional groups, one for aryl carbon to oxygen and one for methyl carbon to oxygen. The aromatic  $C \equiv C$  and  $C-H$  functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The  $CH_3$  and methyl  $C-O$  functional groups are the same as those of the corresponding ether groups given in the corresponding section.

The  $C-O$  functional group comprising the bond between the ether oxygen and aromatic ring is equivalent to that of the methyl ether  $C-O$  functional group except that  $\Delta E_{H_2MO}(AO/HO)$  in Eq. (15.42) and  $E_T(atom-atom,msp^3.AO)$  in Eq. (15.52) are both  $-1.13379 \text{ eV}$  (Eq. (14.247)).  $E_T(atom-atom,msp^3.AO)$  is based on the energy match between the  $OCH_3$  group and the  $C2sp^3$  HO of the aryl group and is twice that of the aryl  $C-H$  group that it replaces.

The symbols of the functional groups of anisole are given in Table 15.261. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of anisole are given in Tables 15.262, 15.263, and 15.264, respectively. The total energy of anisole given in Table 15.265 was calculated as the sum over the integer multiple of each  $E_D(Grp)$  of Table 15.264 corresponding to functional-group composition of the molecule. The bond angle parameters of anisole determined using Eqs. (15.79-15.108) are given in Table 15.266.

Table 15.261. The symbols of functional groups of anisole.

| Functional Group   | Group Symbol     |
|--------------------|------------------|
| CC (aromatic bond) | $C \equiv C$     |
| CH (aromatic)      | $CH$ (i)         |
| Aryl C-O           | $C-O$ (a)        |
| Methyl C-O         | $C-O$ (b)        |
| $CH_3$ group       | $C-H$ ( $CH_3$ ) |



Table 15.262. The geometrical bond parameters of anisole and experimental values [1].

| Parameter                        | C=C Group  | C-H (i) Group | C-O (a) Group | C-O (b) Group | C-H (CH <sub>3</sub> ) Group |
|----------------------------------|------------|---------------|---------------|---------------|------------------------------|
| $a$ (Å)                          | 1.47348    | 1.60061       | 1.82682       | 1.80717       | 1.64920                      |
| $c'$ (Å)                         | 1.31468    | 1.03299       | 1.35160       | 1.34431       | 1.04836                      |
| Bond Length<br>$2c'$ (Å)         | 1.39140    | 1.09327       | 1.43047       | 1.42276       | 1.10974                      |
| Exp. Bond Length<br>(phenol) (Å) | 1.397 avg. | 1.084         |               |               | 1.11 (avg.)                  |
|                                  | (phenol)   |               |               |               | (toluene)                    |
| $b_1 c'$ (Å)                     | 0.66540    | 1.22265       | 1.22900       | 1.20776       | 1.27295                      |
| $e$                              | 0.89223    | 0.64537       | 0.75986       | 0.74388       | 0.63580                      |

Table 15.263. The MO to HO intercept geometrical bond parameters of anisole.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{msp}, AO)$ .

| Bond                                                                          | Atom           | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy C2sp <sup>2</sup> (eV) | $r_{\text{final}}$ (Å) | $E_{\text{total}}(\text{C2sp}^2)$ (eV) Final | $E(\text{C2sp}^2)$ (eV) Final | $\theta'$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ (Å) | $d_2$ (Å) |
|-------------------------------------------------------------------------------|----------------|-------------------|-------------------|-------------------|-------------------|-------------------------------------------|------------------------|----------------------------------------------|-------------------------------|---------------|----------------|----------------|-----------|-----------|
| C'-H (C <sub>1</sub> H)                                                       | C'             | -0.85035          | -0.85035          | -0.56690          | 0                 | -153.88327                                | 0.91771                | -17.09334                                    | -16.90248                     | 74.42         | 105.38         | 38.84          | 1.24678   | 0.21379   |
| C'-H (OC <sub>1</sub> H <sub>3</sub> )                                        | C'             | -0.72457          | 0                 | 0                 | 0                 | -152.34026                                | 0.91771                | -15.53033                                    | -15.35946                     | 78.85         | 101.15         | 42.40          | 1.21777   | 0.16921   |
| (C <sub>6</sub> ) <sub>2</sub> C <sub>6</sub> O-C <sub>6</sub> H <sub>5</sub> | C <sub>6</sub> | -0.72457          | 0                 | 0                 | 0                 | -152.34026                                | 0.91771                | -15.53033                                    | -15.35946                     | 95.98         | 84.02          | 46.10          | 1.25319   | 0.09112   |
| (C <sub>6</sub> ) <sub>2</sub> C <sub>6</sub> O-C <sub>6</sub> H <sub>5</sub> | O              | -0.72457          | -0.56690          | 0                 | 0                 |                                           | 1.00000                | -16.11722                                    |                               | 93.38         | 86.62          | 44.25          | 1.29456   | 0.04975   |
| (C <sub>6</sub> ) <sub>2</sub> C <sub>6</sub> -OC <sub>6</sub> H <sub>5</sub> | C <sub>6</sub> | -0.56690          | -0.85035          | -0.85035          | 0                 | -153.88327                                | 0.91771                | -17.09334                                    | -16.90248                     | 87.00         | 93.00          | 40.30          | 1.39529   | 0.04170   |
| (C <sub>6</sub> ) <sub>2</sub> C <sub>6</sub> -OC <sub>6</sub> H <sub>5</sub> | O              | -0.56690          | -0.72457          | 0                 | 0                 |                                           | 1.00000                | -16.11722                                    |                               | 91.59         | 88.41          | 43.36          | 1.32814   | 0.02346   |
| (C <sub>6</sub> ) <sub>2</sub> C <sub>6</sub> OC <sub>6</sub> H <sub>5</sub>  | C <sub>6</sub> | -0.56690          | -0.85035          | -0.85035          | 0                 | -153.88327                                | 0.91771                | -17.09334                                    | -16.90248                     | 134.24        | 45.76          | 58.98          | 0.75935   | 0.55533   |
| (C <sub>6</sub> ) <sub>2</sub> C <sub>6</sub> OC <sub>6</sub> H <sub>5</sub>  | C <sub>6</sub> | -0.85035          | -0.85035          | -0.56690          | 0                 | -153.88327                                | 0.91771                | -17.09334                                    | -16.90248                     | 134.24        | 45.76          | 58.98          | 0.75935   | 0.55533   |

Table 15.264. The energy parameters (eV) of functional groups of anisole.

| Parameters                                                     | C=C<br>Group    | CH (i)<br>Group         | C-O (a)<br>Group | C-O (b)<br>Group | CH <sub>3</sub><br>Group  |
|----------------------------------------------------------------|-----------------|-------------------------|------------------|------------------|---------------------------|
| $f_i$                                                          | 0.75            | 1                       |                  |                  |                           |
| $n_1$                                                          | 2               | 1                       | 1                | 1                | 3                         |
| $n_2$                                                          | 0               | 0                       | 0                | 0                | 2                         |
| $n_3$                                                          | 0               | 0                       | 0                | 0                | 0                         |
| $C_1$                                                          | 0.5             | 0.75                    | 0.5              | 0.5              | 0.75                      |
| $C_2$                                                          | 0.85252         | 1                       | 1                | 1                | 1                         |
| $c_1$                                                          | 1               | 1                       | 1                | 1                | 1                         |
| $c_2$                                                          | 0.85252         | 0.91771                 | 0.85395          | 0.85395          | 0.91771                   |
| $c_3$                                                          | 0               | 1                       | 0                | 0                | 0                         |
| $c_4$                                                          | 3               | 1                       | 2                | 2                | 1                         |
| $c_5$                                                          | 0               | 1                       | 0                | 0                | 3                         |
| $C_{10}$                                                       | 0.5             | 0.75                    | 0.5              | 0.5              | 0.75                      |
| $C_{100}$                                                      | 0.85252         | 1                       | 1                | 1                | 1                         |
| $V_r$ (eV)                                                     | -101.12679      | -37.10024               | -32.67197        | -33.15757        | -107.32728                |
| $V_p$ (eV)                                                     | 20.69825        | 13.17125                | 10.06645         | 10.12103         | 38.92728                  |
| $T$ (eV)                                                       | 34.31559        | 11.58941                | 8.94231          | 9.17389          | 32.53914                  |
| $V_m$ (eV)                                                     | -17.15779       | -5.79470                | -4.47115         | -4.58695         | -16.26957                 |
| $E_{\text{atom}}(\text{eV})$                                   | 0               | -14.63489               | -14.63489        | -14.63489        | -15.56407                 |
| $\Delta E_{H_{1s}, \text{atom}}(\text{eV})$                    | 0               | -1.13379                | -1.13379         | -1.44915         | 0                         |
| $E_r(\text{atom})$ (eV)                                        | 0               | -13.50110               | -13.50110        | -13.18574        | -15.56407                 |
| $E_r(\mu_{1s})$ (eV)                                           | -63.27075       | -31.63539               | -31.63547        | -31.63533        | -67.69451                 |
| $E_r(\text{atom} - \text{atom}, \text{msp}^3, \text{AO})$ (eV) | -2.26759        | -0.56690                | -1.13379         | -1.44915         | 0                         |
| $E_r(\text{eV})$                                               | -65.53833       | -32.20226               | -32.76916        | -33.08452        | -67.69450                 |
| $\omega$ ( $10^{15}$ rad/s)                                    | 49.7272         | 26.4826                 | 11.8393          | 12.0329          | 24.9286                   |
| $E_s$ (eV)                                                     | 32.73133        | 17.43132                | 7.79284          | 7.92028          | 16.40846                  |
| $\bar{E}_b$ (eV)                                               | -0.35806        | -0.26130                | -0.18097         | -0.18420         | -0.25352                  |
| $\bar{E}_{\text{vib}}$ (eV)                                    | 0.19649<br>[49] | 0.35532<br>Eq. (13.458) | 0.13663<br>[21]  | 0.13663<br>[21]  | 0.35532<br>(Eq. (13.458)) |
| $\bar{E}_{\text{elec}}$ (eV)                                   | -0.25982        | -0.08364                | -0.11266         | -0.11589         | -0.22757                  |
| $E_{\text{mag}}$ (eV)                                          | 0.14803         | 0.14803                 | 0.14803          | 0.14803          | 0.14803                   |
| $E_r(\text{ioniz})$ (eV)                                       | -49.54347       | -32.28590               | -32.88182        | -33.20040        | -67.92207                 |
| $E_{\text{ioniz}}(r, \text{ioniz})$ (eV)                       | -14.63489       | -14.63489               | -14.63489        | -14.63489        | -14.63489                 |
| $E_{\text{ioniz}}(r, \text{ioniz})$ (eV)                       | 0               | -13.59844               | 0                | 0                | -13.59844                 |
| $E_p(\text{ioniz})$ (eV)                                       | 5.63881         | 3.90454                 | 3.61204          | 3.93062          | 12.49186                  |

Table 15.265. The total bond energies of anisole calculated using the functional group composition and the energies of Table 15.264 compared to the experimental values [2].

| Formula                        | Name    | $\text{C}^\bullet\text{C}^\bullet$ | $\text{C}^\bullet\text{H}$ (i) | $\text{C}^\bullet\text{O}$ (a) | $\text{C}^\bullet\text{O}$ (b) | $\text{CH}_3$ Group | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|--------------------------------|---------|------------------------------------|--------------------------------|--------------------------------|--------------------------------|---------------------|-----------------------------------|-------------------------------------|----------------|
| $\text{C}_6\text{H}_5\text{O}$ | Anisole | 6                                  | 5                              | 1                              | 1                              | 1                   | 73.3906                           | 73.355                              | -0.0047        |

Table 15.266. The bond angle parameters of anisole and experimental values [1].  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{mp}^2, \text{AO})$ .

| Atoms of Angle                | $2c^\bullet$ Bond 1 ( $a_1$ ) | $2c^\bullet$ Bond 2 ( $a_2$ ) | $2c^\bullet$ Terminal Atoms ( $a_3$ ) | $E_{\text{calculated}}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3 A) | $E_{\text{calculated}}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3 A) | $c_2$ Atom 1 | $c_2$ Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_2'$  | $E_T$ (eV) | $\theta_1$ ( $^\circ$ ) | $\theta_2$ ( $^\circ$ ) | Cal. $\theta$ ( $^\circ$ ) | Exp. $\theta$ ( $^\circ$ ) |
|-------------------------------|-------------------------------|-------------------------------|---------------------------------------|--------------------------------|-------------------------------------------------|--------------------------------|-------------------------------------------------|--------------|--------------|-------|-------|-------|---------|------------|-------------------------|-------------------------|----------------------------|----------------------------|
| $\angle\text{CCC}$ (aromatic) | 2.62936                       | 2.62936                       | 4.585                                 | -17.17218                      | 34                                              | -17.17218                      | 34                                              | 0.79232      | 0.79232      | 1     | 1     | 1     | 0.79232 | -1.83836   |                         |                         | 120.19                     | 120 [50-52] (benzene)      |
| $\angle\text{CCH}$ (aromatic) |                               |                               |                                       |                                |                                                 |                                |                                                 |              |              |       |       |       |         |            |                         |                         | 119.91                     | 120 [50-52] (benzene)      |

## PYRROLE

Pyrrole having the formula  $C_4H_5N$  comprises the conjugated alkene 1,3-butdiene that forms a cyclic structure by terminal-atom bonding to a  $NH$  functional group. The two symmetrical carbon-to-nitrogen bonds comprise the  $C-N-C$  functional group. The 1,3-butdiene moiety comprises  $C-C$ ,  $C=C$ , and  $CH$  functional groups. The  $C-C$  and  $C=C$  groups are equivalent to the corresponding groups of 1,3-butdiene given in the Cyclic and Conjugated Alkenes section except that the energies terms of the corresponding to oscillation in the transition state match pyrrole. Furthermore, the conjugated double bonds have the same bonding as in 1,3-butdiene except that the hybridization terms  $c_2$  of the  $C-C$  and  $C=C$  groups and  $C_2$  and  $C_{2o}$  of the  $C=C$  group in Eqs. (15.42) and (15.52) become that of benzene given by Eq. (15.143),  $(C_2(benzeneC2sp^3HO) = c_2(benzeneC2sp^3HO) = 0.85252)$ , in the cyclic pyrrole MO which has aromatic character. The bonding in pyrrole, furan, and thiophene are the same except for the energy match to the corresponding heteroatoms. The hybridization permits double-bond character in the carbon-heteroatom bonding.

The  $NH$  group is solved equivalently to that of a secondary amine as given in the corresponding section except that the hybridization term  $c_2$  is that of the amino group of aniline in order provide double-bond character to match the group to the other orbitals of the molecule. Similarly, the  $CH$  functional group is equivalent to that of 1,3-butdiene, except that  $\Delta E_{H_2MO}(AO/HO) = -2.26758 \text{ eV}$  (Eq. (14.247)) in Eq. (15.42) in order to provide matching double-bond character.

The solution of the  $C-N-C$  functional group comprises the hybridization of the  $2s$  and  $2p$  AOs of each  $C$  to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  HOs and the nitrogen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. Thus, the  $C-N-C$  bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with  $n_1 = 2$  in Eqs. (15.42) and (15.52). The hybridization factor  $c_2(arylC2sp^3HO \text{ to } N) = 0.84665$  (Eq. (15.152)) matches the double-bond character of the  $C2sp^3$  HOs to the  $N$  atom of the  $NH$  group, and  $C_2$  and  $C_{2o}$  in Eqs. (15.42) and (15.52)

become that of benzene given by Eq. (15.143),  $C_2(\text{benzene}C2sp^3HO) = 0.85252$ . Furthermore,  $\Delta E_{H_2MO}(AO/HO)$  in Eq. (15.42) and  $E_T(\text{atom} - \text{atom}, msp^3.AO)$  in Eq. (15.52) are both  $-0.92918 \text{ eV}$  (Eq. (14.513)) per atom corresponding to  $-3.71673 \text{ eV}$  in total. This is the maximum energy for a single bond and corresponds to methylene character 5 as given in the Continuous-Chain Alkanes section.

The symbols of the functional groups of pyrrole are given in Table 15.267. The structure of pyrrole is shown in Figure 65. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of pyrrole are given in Tables 15.268, 15.269, and 15.270, respectively. The total energy of 10 pyrrole given in Table 15.271 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.270 corresponding to functional-group composition of the molecule. The bond angle parameters of pyrrole determined using Eqs. (15.79-15.108) are given in Table 15.272.

15 Table 15.267. The symbols of functional groups of pyrrole.

| Functional Group        | Group Symbol |
|-------------------------|--------------|
| $C_a = C_b$ double bond | $C = C$      |
| $C_b - C_b$             | $C - C$      |
| $C_a - N - C_a$         | $C - N - C$  |
| NH group                | $NH$         |
| CH                      | $CH$         |

Table 15.268. The geometrical bond parameters of pyrrole and experimental values [1].

| Parameter                               | C = C<br>Group     | C - C<br>Group     | C - N - C<br>Group | NH<br>Group        | CH<br>Group        |
|-----------------------------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| $a$ ( $a_0$ )                           | 1.45103            | 1.77965            | 1.43222            | 1.24428            | 1.53380            |
| $c'$ ( $a_0$ )                          | 1.30463            | 1.33404            | 1.29614            | 0.94134            | 1.01120            |
| Bond Length<br>$2c'$ ( $\text{\AA}$ )   | 1.38076            | 1.41188            | 1.37178            | 0.996270           | 1.07021            |
| Exp. Bond<br>Length<br>( $\text{\AA}$ ) | 1.382<br>(pyrrole) | 1.417<br>(pyrrole) | 1.370<br>(pyrrole) | 0.996<br>(pyrrole) | 1.076<br>(pyrrole) |
| $b, c$ ( $a_0$ )                        | 0.63517            | 1.17792            | 0.60931            | 0.81370            | 1.15326            |
| $e$                                     | 0.89910            | 0.74961            | 0.90499            | 0.75653            | 0.65928            |

Table 15.269. The MO to HO intercept geometrical bond parameters of pyrrole.  $R_i$  is an alkyl group and  $R, R', R''$  are H or alkyl groups.  $E_T$  is  $E_T(atom - atom, msp, AO)$ .

| Bond                 | Atom | $E_T$<br>(eV)<br>Bond 1 | $E_T$<br>(eV)<br>Bond 2 | $E_T$<br>(eV)<br>Bond 3 | $E_T$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>C2sp <sup>3</sup><br>(eV) | $r_{bond}$<br>(a <sub>0</sub> ) | $E_{bond}$ (C2sp <sup>3</sup> )<br>(eV)<br>Final | $E$ (C2sp <sup>3</sup> )<br>(eV)<br>Final | $\theta^*$<br>(°) | $\theta_1$<br>(°) | $\theta_2$<br>(°) | $d_1$<br>(a <sub>0</sub> ) | $d_2$<br>(a <sub>0</sub> ) |
|----------------------|------|-------------------------|-------------------------|-------------------------|-------------------------|----------------------------------------------------|---------------------------------|--------------------------------------------------|-------------------------------------------|-------------------|-------------------|-------------------|----------------------------|----------------------------|
| C'-H (C'H)           | C'   | -1.13380                | -0.92918                | 0                       | 0                       | -153.67867                                         | 0.91771                         | -16.88873                                        | -16.69786                                 | 83.33             | 96.65             | 43.94             | 1.10452                    | 0.09331                    |
| C'-H (C'H)           | C'   | -1.13380                | -1.13380                | 0                       | 0                       | -153.88328                                         | 0.91771                         | -17.09334                                        | -16.90248                                 | 82.21             | 97.79             | 43.14             | 1.11914                    | 0.10794                    |
| C'-C(H)C'-C'(H)C'-C' | C'   | -1.13380                | -1.13380                | 0                       | 0                       | -153.88328                                         | 0.91771                         | -17.09334                                        | -16.90248                                 | 91.37             | 88.43             | 42.49             | 1.31226                    | 0.02177                    |
| C'-C(H)C'(H)C'-C'    | C'   | -1.13380                | -1.13380                | 0                       | 0                       | -153.88328                                         | 0.91771                         | -17.09334                                        | -16.90248                                 | 136.36            | 43.64             | 59.86             | 0.72837                    | 0.57606                    |
| HNC'-C'(H)           | C'   | -1.13380                | -0.92918                | 0                       | 0                       | -153.67867                                         | 0.91771                         | -16.88873                                        | -16.69786                                 | 136.75            | 43.25             | 60.35             | 0.71784                    | 0.38678                    |
| C'(H)N-C'-C'(H)      | C'   | -1.13380                | -0.92918                | 0                       | 0                       | -153.67867                                         | 0.91771                         | -16.88873                                        | -16.69786                                 | 138.54            | 41.46             | 61.09             | 0.69238                    | 0.60376                    |
| C'(H)N-C'-C'(H)      | N    | -0.92918                | -0.92918                | 0                       | 0                       |                                                    | 0.93084                         | -16.68411                                        |                                           | 138.92            | 41.08             | 61.59             | 0.68147                    | 0.61467                    |
| N-H (NH)             | N    | -0.92918                | -0.92918                | 0                       | 0                       |                                                    | 0.93084                         | -16.68411                                        |                                           | 117.34            | 62.66             | 62.90             | 0.56678                    | 0.37456                    |

Table 15.270. The energy parameters (eV) of functional groups of pyrrole.

| Parameters                                      | C = C<br>Group | C - C<br>Group  | C - N - C<br>Group | NH<br>Group     | CH<br>Group     |
|-------------------------------------------------|----------------|-----------------|--------------------|-----------------|-----------------|
| $n_1$                                           | 2              | 1               | 2                  | 1               | 1               |
| $n_2$                                           | 0              | 0               | 0                  | 0               | 0               |
| $n_3$                                           | 0              | 0               | 0                  | 0               | 0               |
| $C_1$                                           | 0.5            | 0.5             | 0.5                | 0.75            | 0.75            |
| $C_2$                                           | 0.85252        | 1               | 0.85252            | 0.93613         | 1               |
| $c_1$                                           | 1              | 1               | 1                  | 0.75            | 1               |
| $c_2$                                           | 0.85252        | 0.85252         | 0.84665            | 0.92171         | 0.91771         |
| $c_3$                                           | 0              | 0               | 0                  | 1               | 1               |
| $c_4$                                           | 4              | 2               | 4                  | 1               | 1               |
| $c_5$                                           | 0              | 0               | 0                  | 1               | 1               |
| $C_{10}$                                        | 0.5            | 0.5             | 0.5                | 0.75            | 0.75            |
| $C_{20}$                                        | 0.85252        | 1               | 0.85252            | 1               | 1               |
| $V_e$ (eV)                                      | -104.37986     | -33.80733       | -106.58684         | -39.48897       | -39.09538       |
| $V_p$ (eV)                                      | 20.85777       | 10.19898        | 20.99432           | 14.45367        | 13.45505        |
| $T$ (eV)                                        | 35.96751       | 9.49831         | 37.21047           | 15.86820        | 12.74462        |
| $V_m$ (eV)                                      | -17.98376      | -4.74915        | -18.60523          | -7.93410        | -6.37231        |
| $E(\text{AOIHO})$ (eV)                          | 0              | -14.63489       | 0                  | -14.53414       | -14.63489       |
| $\Delta E_{H_2MO}(\text{AOIHO})$ (eV)           | -2.26759       | -1.85836        | -3.71673           | 0               | -2.26758        |
| $E_r(\text{AOIHO})$ (eV)                        | 2.26759        | -12.77653       | 3.71673            | -14.53414       | -12.36731       |
| $E_r(H_2MO)$ (eV)                               | -63.27075      | -31.63572       | -63.27056          | -31.63534       | -31.63533       |
| $E_r(\text{atom} - \text{atom}, msp^3 AO)$ (eV) | -2.26759       | -2.26759        | -3.71673           | 0               | 0               |
| $E_r(MO)$ (eV)                                  | -65.53833      | -33.90295       | -66.98746          | -31.63537       | -31.63537       |
| $\omega$ ( $10^{13}$ rad / s)                   | 15.4421        | 12.3131         | 15.7474            | 48.7771         | 28.9084         |
| $E_K$ (eV)                                      | 10.16428       | 8.10471         | 10.36521           | 32.10594        | 19.02803        |
| $\bar{E}_D$ (eV)                                | -0.20668       | -0.19095        | -0.21333           | -0.35462        | -0.27301        |
| $\bar{E}_{Kvib}$ (eV)                           | 0.17897<br>[6] | 0.14829<br>[48] | 0.11159<br>[12]    | 0.40696<br>[24] | 0.39427<br>[56] |
| $\bar{E}_{osc}$ (eV)                            | -0.11720       | -0.11680        | -0.15754           | -0.15115        | -0.07587        |
| $E_{mag}$ (eV)                                  | 0.14803        | 0.14803         | 0.14803            | 0.14803         | 0.14803         |
| $E_r(\text{Group})$ (eV)                        | -65.77272      | -34.01976       | -67.30254          | -31.78651       | -31.71124       |
| $E_{initial}(c_1 \text{ AOIHO})$ (eV)           | -14.63489      | -14.63489       | -14.63489          | -14.53414       | -14.63489       |
| $E_{initial}(c_2 \text{ AOIHO})$ (eV)           | 0              | 0               | 0                  | -13.59844       | -13.59844       |
| $E_p(\text{Group})$ (eV)                        | 7.23317        | 4.74998         | 8.76298            | 3.51208         | 3.32988         |



Table 15.271. The total bond energies of pyrrole calculated using the functional group composition and the energies of Table 15.270 compared to the experimental values [2].

| Formula   | Name    | $C-C$                             | $C-N-C$ | $NH$                                | $CH$ |
|-----------|---------|-----------------------------------|---------|-------------------------------------|------|
| $C_4H_5N$ | Pyrrole | 2                                 | 1       | 1                                   | 4    |
|           |         | Calculated Total Bond Energy (eV) |         | Experimental Total Bond Energy (eV) |      |
|           |         | 44.81090                          |         | 44.785                              |      |
|           |         |                                   |         | Relative Error                      |      |
|           |         |                                   |         | -0.00057                            |      |

Table 15.272. The bond angle parameters of pyrrole and experimental values [1]. In the calculation of  $\theta_i$ , the parameters from the preceding angle were used.  $E_r$  is  $E_r(atom - atom, exp, AC)$ .

| Atoms of Angle      | $2C^1$<br>Bond 1<br>( $\sigma_b$ ) | $2C^2$<br>Bond 2<br>( $\sigma_b$ ) | $2C^3$<br>Terminal<br>Atoms<br>( $\sigma_a$ ) | $E_{r,calc}$<br>Atom 1 | Atom 1<br>Hybridization<br>Designation<br>(Table 15.3.B) | $E_{r,calc}$<br>Atom 2 | Atom 2<br>Hybridization<br>Designation<br>(Table 15.3.B) | $C_1$ | $C_2$<br>Atom 1              | $C_3$ | $C_4$ | $C_5$   | $E_T$<br>(eV) | $\theta_r$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | Calc. $\theta$<br>( $^\circ$ ) | Exp. $\theta$<br>( $^\circ$ ) |
|---------------------|------------------------------------|------------------------------------|-----------------------------------------------|------------------------|----------------------------------------------------------|------------------------|----------------------------------------------------------|-------|------------------------------|-------|-------|---------|---------------|----------------------------|----------------------------|----------------------------|--------------------------------|-------------------------------|
| $\angle HC-N$       | 2.02241                            | 2.59228                            | 4.0166                                        | -14.42575              | I                                                        | -14.53414              | N                                                        | 0.75  | 0.91771                      | I     | 0.75  | 1.00435 | 0             |                            |                            |                            | 120.51                         | 121.5<br>(pyrrole)            |
| $\angle C-C^*H_a$   |                                    |                                    |                                               |                        |                                                          |                        |                                                          |       |                              |       |       |         |               |                            | 120.51                     | 107.52                     | 131.97                         |                               |
| $\angle HNC_a$      | 1.88268                            | 2.59228                            | 3.9897                                        | -14.55414              | N                                                        | -16.49325              | 6                                                        | 0.75  | 0.84665<br>(Eq.<br>(15.152)) | I     | 0.75  | 0.97435 | 0             |                            |                            |                            | 120.37                         |                               |
| $\angle HC^*C^*C^*$ | 2.02241                            | 2.68007                            | 4.2111                                        | -16.88073<br>$C_b$     | 15                                                       | -15.95954<br>$C^*$     | 6                                                        | 0.75  | 0.80561                      | I     | 0.75  | 1.05822 | 0             |                            |                            |                            | 127.20                         | 127.1<br>(pyrrole)            |
| $\angle HC^*C^*C^*$ | 2.02241                            | 2.60925                            | 4.2111                                        | -16.88073<br>$C_a$     | 15                                                       | -15.95954<br>$C_b$     | 6                                                        | 0.75  | 0.80561                      | I     | 0.75  | 1.05822 | 0             |                            |                            |                            | 130.36                         |                               |
| $\angle HC^*C^*C^*$ | 2.02241                            | 2.60925                            | 4.1312                                        | -17.09334<br>$C_b$     | 18                                                       | -16.47951<br>$C^*$     | 11                                                       | 0.75  | 0.79597                      | I     | 0.75  | 1.03725 | 0             |                            |                            |                            | 123.76                         |                               |
| $\angle C^*C^*H_b$  |                                    |                                    |                                               |                        |                                                          |                        |                                                          |       |                              |       |       |         |               |                            |                            |                            | 127.23                         | 127.1<br>(pyrrole)            |
| $\angle NC^*C^*$    | 2.59228                            | 2.60925                            | 4.1952                                        | -14.55414              | N                                                        | -17.09334<br>$C_b$     | 18                                                       | I     | 0.79597<br>(Eq.<br>(15.152)) | I     | I     | 0.82131 | -1.44915      |                            |                            |                            | 107.52                         | 107.7<br>(pyrrole)            |
| $\angle C^*NC_a$    | 2.59228                            | 2.59228                            | 4.2426                                        | -17.81791              | 26                                                       | -17.81791              | 26                                                       | I     | 0.76360                      | I     | I     | 0.76360 | -1.83536      |                            |                            |                            | 109.33                         | 109.8<br>(pyrrole)            |
| $\angle C^*C^*C^*$  | 2.60925                            | 2.68007                            | 4.2426                                        | -17.81791              | 26                                                       | -18.02252              | 29                                                       | I     | 0.76360                      | I     | I     | 0.75927 | -1.83536      |                            |                            |                            | 107.01                         | 107.4<br>(pyrrole)            |

## FURAN

Furan having the formula  $C_4H_4O$  comprises the conjugated alkene 1,3-butdiene that forms a cyclic structure by terminal-atom bonding to an oxygen atom. The two symmetrical carbon-to-oxygen bonds comprise the  $C-O-C$  functional group. The 1,3-butdiene moiety  
5 comprises  $C-C$ ,  $C=C$ , and  $CH$  functional groups. The  $CH$ ,  $C-C$ , and  $C=C$  groups are equivalent to the corresponding groups of pyrrole given in the corresponding section.

The  $C-O-C$  functional group of furan is solved in a similar manner as that of the  $C-N-C$  group of pyrrole. The solution of the  $C-O-C$  functional group comprises the hybridization of the  $2s$  and  $2p$  AOs of each  $C$  to form a single  $2sp^3$  shell as an energy  
10 minimum, and the sharing of electrons between two  $C2sp^3$  HOs and the oxygen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. Thus, the  $C-O-C$ -bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with  $n_1 = 2$  in Eqs. (15.42) and (15.52). The hybridization factor  $c_2(\text{aryl}C2sp^3HO \text{ to } O) = 0.79329$  (Eq. (15.150)) matches the double-  
15 bond character of the  $C2sp^3$  HOs to the  $O$  atom, and  $C_2$  and  $C_{2o}$  in Eqs. (15.42) and (15.52) become that of benzene given by Eq. (15.143),  $C_2(\text{benzene}C2sp^3HO) = 0.85252$ . Furthermore,  $E_T(\text{atom-atom}, msp^3.AO)$  in Eq. (15.52) is  $-0.92918 \text{ eV}$  (Eq. (14.513)) per atom corresponding to  $-3.71673 \text{ eV}$  in total.

The symbols of the functional groups of furan are given in Table 15.273. The  
20 structure of furan is shown in Figure 66. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of furan are given in Tables 15.274, 15.275, and 15.276, respectively. The total energy of furan given in Table 15.277 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.276 corresponding to functional-group composition of the molecule.  
25 The bond angle parameters of furan determined using Eqs. (15.79-15.108) are given in Table 15.278.

Table 15.273. The symbols of functional groups of furan.

| Functional Group        | Group Symbol |
|-------------------------|--------------|
| $C_s = C_s$ double bond | $C = C$      |
| $C_s - C_s$             | $C - C$      |
| $C_s - O - C_s$         | $C - O - C$  |
| $CH$                    | $CH$         |

Table 15.274. The geometrical bond parameters of furan and experimental values [1].

| Parameter                         | $C = C$       | $C - C$       | $C - O - C$   | $CH$          |
|-----------------------------------|---------------|---------------|---------------|---------------|
| $a$ ( $a_0$ )                     | 1.45103       | 1.77965       | 1.41546       | 1.53380       |
| $c'$ ( $a_0$ )                    | 1.30463       | 1.33404       | 1.28854       | 1.01120       |
| Bond Length                       | 1.38076       | 1.41188       | 1.36373       | 1.07021       |
| Exp. Bond Length ( $\text{\AA}$ ) | 1.361 (furan) | 1.431 (furan) | 1.362 (furan) | 1.075 (furan) |
| $h, c$ ( $a_0$ )                  | 0.63517       | 1.17792       | 0.58583       | 1.15326       |
| $e$                               | 0.89910       | 0.74961       | 0.91033       | 0.65928       |

Table 15.275. The MO to HO intercept geometrical bond parameters of furan.  $R_i$  is an alkyl group and  $R, R', R''$  are  $H$  or alkyl groups.  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{msp}, AO)$ .

| Bond                          | Atom  | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C2sp^3$ (eV) | $r_{\text{final}}$ ( $a_0$ ) | $E_{\text{coreval}}(C2sp^3)$ (eV) Final | $E(C2sp^3)$ (eV) Final | $\theta^*$ ( $^\circ$ ) | $\theta_1$ ( $^\circ$ ) | $\theta_2$ ( $^\circ$ ) | $d_1$ ( $a_0$ ) | $d_2$ ( $a_0$ ) |
|-------------------------------|-------|-------------------|-------------------|-------------------|-------------------|----------------------------------|------------------------------|-----------------------------------------|------------------------|-------------------------|-------------------------|-------------------------|-----------------|-----------------|
| $C-H$ ( $C_sH$ )              | $C_s$ | -1.13380          | -0.92918          | 0                 | 0                 | -153.67867                       | 0.91771                      | -16.88873                               | -16.69786              | 83.35                   | 96.65                   | 43.94                   | 1.10452         | 0.09331         |
| $C-H$ ( $C_sH$ )              | $C_s$ | -1.13380          | -1.13380          | 0                 | 0                 | -153.88328                       | 0.91771                      | -17.09334                               | -16.90248              | 82.21                   | 97.79                   | 43.14                   | 1.11914         | 0.10794         |
| $C_s = (H)C_s - C_s(H) = C_s$ | $C_s$ | -1.13380          | -1.13380          | 0                 | 0                 | -153.88328                       | 0.91771                      | -17.09334                               | -16.90248              | 91.57                   | 88.43                   | 42.49                   | 1.31226         | 0.02177         |
| $C_s = C_s(H)(H)C_s = C_s$    | $C_s$ | -1.13380          | -1.13380          | 0                 | 0                 | -153.88328                       | 0.91771                      | -17.09334                               | -16.90248              | 136.36                  | 43.64                   | 59.86                   | 0.72857         | 0.57606         |
| $OC_s = C_s(H)$               | $C_s$ | -1.13380          | -0.92918          | 0                 | 0                 | -153.67867                       | 0.91771                      | -16.88873                               | -16.69786              | 136.75                  | 43.25                   | 60.35                   | 0.71784         | 0.58678         |
| $C_sO - C_s = C_s(H)$         | $C_s$ | -1.13380          | -0.92918          | 0                 | 0                 | -153.67867                       | 0.91771                      | -16.88873                               | -16.69786              | 140.16                  | 39.84                   | 61.75                   | 0.66992         | 0.61862         |
| $C_sO - C_s = C_s(H)$         | $O$   | -0.92918          | -0.92918          | 0                 | 0                 | -153.67867                       | 1.00000                      | -16.68411                               |                        | 140.52                  | 39.48                   | 62.25                   | 0.65906         | 0.62947         |

Table 15.276. The energy parameters (eV) of functional groups of furan.

| Parameters                        | C = C<br>Group | C - C<br>Group  | C - O - C<br>Group | CH<br>Group     |
|-----------------------------------|----------------|-----------------|--------------------|-----------------|
| $n_1$                             | 2              | 1               | 2                  | 1               |
| $n_2$                             | 0              | 0               | 0                  | 0               |
| $n_3$                             | 0              | 0               | 0                  | 0               |
| $C_1$                             | 0.5            | 0.5             | 0.5                | 0.75            |
| $C_2$                             | 0.85252        | 1               | 0.85252            | 1               |
| $c_1$                             | 1              | 1               | 1                  | 1               |
| $c_2$                             | 0.85252        | 0.85252         | 0.79329            | 0.91771         |
| $c_3$                             | 0              | 0               | 0                  | 1               |
| $c_4$                             | 4              | 2               | 4                  | 1               |
| $c_5$                             | 0              | 0               | 0                  | 1               |
| $C_{1a}$                          | 0.5            | 0.5             | 0.5                | 0.75            |
| $C_{2a}$                          | 0.85252        | 1               | 0.85252            | 1               |
| $V_e$ (eV)                        | -104.37986     | -33.80733       | -102.49036         | -39.09538       |
| $V_p$ (eV)                        | 20.85777       | 10.19898        | 21.11822           | 13.45505        |
| $T$ (eV)                          | 35.96751       | 9.49831         | 36.20391           | 12.74462        |
| $V_m$ (eV)                        | -17.98376      | -4.74915        | -18.10196          | -6.37231        |
| $E_{(AO/HO)}$ (eV)                | 0              | -14.63489       | 0                  | -14.63489       |
| $\Delta E_{H_2MO(AO/HO)}$ (eV)    | -2.26759       | -1.85836        | 0                  | -2.26758        |
| $E_T(AO/HO)$ (eV)                 | 2.26759        | -12.77653       | 0                  | -12.36731       |
| $E_T(H_2MO)$ (eV)                 | -63.27075      | -31.63572       | -63.27019          | -31.63533       |
| $E_T(atom - atom, msp^3.AO)$ (eV) | -2.26759       | -2.26759        | -3.71673           | 0               |
| $E_T(MO)$ (eV)                    | -65.53833      | -33.90295       | -66.98746          | -31.63537       |
| $\omega$ ( $10^{15}$ rad / s)     | 15.4421        | 12.3131         | 58.0664            | 28.9084         |
| $E_K$ (eV)                        | 10.16428       | 8.10471         | 38.22034           | 19.02803        |
| $\bar{E}_D$ (eV)                  | -0.20668       | -0.19095        | -0.40965           | -0.27301        |
| $\bar{E}_{Kvib}$ (eV)             | 0.17897<br>[6] | 0.14829<br>[48] | 0.12523<br>[57]    | 0.39427<br>[56] |
| $\bar{E}_{usc}$ (eV)              | -0.11720       | -0.11680        | -0.34704           | -0.07587        |
| $E_{mag}$ (eV)                    | 0.14803        | 0.14803         | 0.14803            | 0.14803         |
| $E_T(group)$ (eV)                 | -65.77272      | -34.01976       | -67.68154          | -31.71124       |
| $E_{initial}(c_4 AO/HO)$ (eV)     | -14.63489      | -14.63489       | -14.63489          | -14.63489       |
| $E_{initial}(c_5 AO/HO)$ (eV)     | 0              | 0               | 0                  | -13.59844       |
| $E_D(group)$ (eV)                 | 7.23317        | 4.74998         | 9.14198            | 3.32988         |

Table 15.277. The total bond energies of furan calculated using the functional group composition and the energies of Table 15.276 compared to the experimental values [2].

| Name                            | C=C        |              | C-C        |              | C-O-C      |              | CH         |              | Total Bond Energy (eV) |              | Relative Error |              |
|---------------------------------|------------|--------------|------------|--------------|------------|--------------|------------|--------------|------------------------|--------------|----------------|--------------|
|                                 | Calculated | Experimental | Calculated | Experimental | Calculated | Experimental | Calculated | Experimental | Calculated             | Experimental | Calculated     | Experimental |
| C <sub>4</sub> H <sub>4</sub> O |            |              |            |              |            |              |            |              | 41.692                 | 41.692       | 0.00033        |              |

Table 15.278. The bond angle parameters of furan and experimental values [1]. In the calculation of  $\theta_v$ , the parameters from the preceding angle were used.  $E_r$  is  $E_r(atom-atom, msp, AO)$ .

| Atoms of Angle     | $2c_1$ Bond 1 ( $\alpha_1$ ) | $2c_2$ Bond 2 ( $\alpha_2$ ) | $2c_3$ Terminal Atom ( $\alpha_3$ ) | $E_{\text{Condonite}} \text{ Atom 1}$ | Atom 1 Hybridization Designation (Table 15.3.B) | $E_{\text{Condonite}} \text{ Atom 2}$ | Atom 2 Hybridization Designation (Table 15.3.B) | $c_2$ Atom 1 | $c_2$ Atom 2         | $C_1$ | $C_2$ | $C_3$ | $c_1$ | $c_2'$  | $E_r$ (eV) | $\theta_v$ ( $^\circ$ ) | $\theta_1$ ( $^\circ$ ) | $\theta_2$ ( $^\circ$ ) | Cal. $\theta$ ( $^\circ$ ) | Exp. $\theta$ ( $^\circ$ ) |
|--------------------|------------------------------|------------------------------|-------------------------------------|---------------------------------------|-------------------------------------------------|---------------------------------------|-------------------------------------------------|--------------|----------------------|-------|-------|-------|-------|---------|------------|-------------------------|-------------------------|-------------------------|----------------------------|----------------------------|
| $\angle HC_2O$     | 2.02241                      | 2.57707                      | 3.9228                              | -16.88873                             | 15                                              | -13.61806                             | O                                               | 0.80561      | 0.79329 Eq. (15.150) | 0.75  | 1     |       | 0.75  | 0.98470 | 0          |                         |                         |                         | 117.02                     | 115.9 (furan)              |
| $\angle C_2C_3H_a$ |                              |                              |                                     |                                       |                                                 |                                       |                                                 |              |                      |       |       |       |       |         |            |                         | 117.02                  | 110.69                  |                            |                            |
| $\angle H_1C_2C_3$ | 2.02241                      | 2.66807                      | 4.2269                              | -16.88873                             | 15                                              | -15.95954                             | $C_b$                                           | 0.80561      | 0.85252              | 0.75  | 1     | 1     | 0.75  | 1.05822 | 0          |                         |                         |                         | 128.09                     | 128.0 (furan)              |
| $\angle H_2C_2C_3$ | 2.02241                      | 2.60925                      | 4.2269                              | -16.88873                             | 15                                              | -15.95954                             | $C_b$                                           | 0.80561      | 0.85252              | 0.75  | 1     | 1     | 0.75  | 1.05822 | 0          |                         |                         |                         | 131.32                     |                            |
| $\angle H_1C_2C_3$ | 2.02241                      | 2.60925                      | 4.1312                              | -17.09334                             | 18                                              | -16.47951                             | $C_a$                                           | 0.79597      | 0.82562              | 0.75  | 1     | 1     | 0.75  | 1.03725 | 0          |                         |                         |                         | 125.76                     |                            |
| $\angle C_2C_3H_b$ |                              |                              |                                     |                                       |                                                 |                                       |                                                 |              |                      |       |       |       |       |         |            |                         | 125.76                  | 107.01                  | 127.23                     | 128.0 (furan)              |
| $\angle C_2C_3O$   | 2.60925                      | 2.57707                      | 4.2661                              | -17.09334                             | 18                                              | -13.61806                             | O                                               | 0.79597      | 0.79329 Eq. (15.150) | 1     | 1     | 1     | 1     | 0.79463 | -1.65376   |                         |                         |                         | 110.69                     | 110.7 (furan)              |
| $\angle C_2OC_a$   | 2.57707                      | 2.57707                      | 4.1231                              | -18.22713                             | 30                                              | -18.22713                             | 30                                              | 0.74646      | 0.74646              | 1     | 1     | 1     | 1     | 0.74646 | -1.85836   |                         |                         |                         | 106.25                     | 106.6 (furan)              |
| $\angle C_2C_3C_b$ | 2.60925                      | 2.66807                      | 4.2426                              | -17.81791                             | 26                                              | -18.02252                             | 29                                              | 0.76360      | 0.75493              | 1     | 1     | 1     | 1     | 0.75927 | -1.85836   |                         |                         |                         | 107.01                     | 106.1 (furan)              |

## THIOPHENE

Thiophene having the formula  $C_4H_4S$  comprises the conjugated alkene 1,3-butdiene that forms a cyclic structure by terminal-atom bonding to an oxygen atom. The two symmetrical carbon-to-oxygen bonds comprise the  $C-S-C$  functional group. The 1,3-butdiene moiety  
5 comprises  $C-C$ ,  $C=C$ , and  $CH$  functional groups. The  $CH$ ,  $C-C$ , and  $C=C$  groups are equivalent to the corresponding groups of pyrrole and furan given in the corresponding sections.

The  $C-S-C$  functional group of thiophene is solved in a similar manner as that of the  $C-N-C$  group of pyrrole and the  $C-O-C$  group of furan. The solution of the  $C-S-C$  functional group comprises the hybridization of the  $2s$  and  $2p$  AOs of each  $C$  to form a single  
10  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  HOs and the oxygen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. Thus, the  $C-S-C$ -bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with  $n_1 = 2$  in Eqs. (15.42) and (15.52).

In thiophene, the energy of sulfur is less than the Coulombic energy between the electron  
15 and proton of  $H$  given by Eq. (1.243). Thus,  $c_2$  in Eq. (15.52) is  $c_2(\text{benzene } C2sp^3 HO) = 0.85252$  to match the double-bond character of the  $C2sp^3$  HOs, and the energy matching condition is further determined by the  $C_2$  parameter. Using the energy of  $S$ ,  $E(S) = -10.36001 \text{ eV}$  in Eq. (15.68) and the  $C2sp^3$  HO energy of  $E(C, 2sp^3) = -15.76868 \text{ eV}$  (Eq. (15.18) corresponding to  $s = 2$  in Eqs. (15.18-15.20), the  
20 hybridization factor  $C_2$  of Eq. (15.52) for the  $C-S-C$ -bond MO is

$$C_2(S3p \text{ to aryl-type } C2sp^3 HO) = \frac{E(S, 3p)}{E(C, 2sp^3)} = \frac{-10.36001 \text{ eV}}{-15.76868 \text{ eV}} = 0.65700 \quad (15.153)$$

$C_{1o}$  is also given by Eq. (15.153). Furthermore,  $\Delta E_{H_1 MO}(AO / HO)$  of the  $C-S-C$ -bond MO in Eq. (15.42) and  $E_r(\text{atom} - \text{atom}, msp^3 AO)$  in Eq. (15.52) are both  $-0.72457 \text{ eV}$  per atom corresponding to  $-2.89830 \text{ eV}$  in total. The energy contribution equivalent to that of  
25 a methyl group (Eq. (14.151)) and that of the  $C-S$ -bond MO of thiols given in the corresponding section matches the energy of the sulfur atom to the  $C2sp^3$  HOs.

The symbols of the functional groups of thiophene are given in Table 15.279. The structure of thiophene is shown in Figure 67. The geometrical (Eqs. (15.1-15.5) and (15.42)),

intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of thiophene are given in Tables 15.280, 15.281, and 15.282, respectively. The total energy of thiophene given in Table 15.283 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.282 corresponding to functional-group composition of the molecule. The 5 bond angle parameters of thiophene determined using Eqs. (15.79-15.108) are given in Table 15.284.

Table 15.279. The symbols of functional groups of thiophene.

| Functional Group        | Group Symbol |
|-------------------------|--------------|
| $C_a = C_b$ double bond | $C = C$      |
| $C_b - C_b$             | $C - C$      |
| $C_a - S - C_a$         | $C - S - C$  |
| CH                      | CH           |

Table 15.280. The geometrical bond parameters of thiophene and experimental values [1].

| Parameter                               | C=C<br>Group         | C-C<br>Group         | C-S-C<br>Group       | CH<br>Group          |
|-----------------------------------------|----------------------|----------------------|----------------------|----------------------|
| $a$ ( $a_0$ )                           | 1.45103              | 1.77965              | 1.74058              | 1.53380              |
| $c'$ ( $a_0$ )                          | 1.30463              | 1.33404              | 1.62766              | 1.01120              |
| Bond Length<br>$2c'$ ( $\text{\AA}$ )   | 1.38076              | 1.41188              | 1.72264              | 1.07021              |
| Exp. Bond<br>Length<br>( $\text{\AA}$ ) | 1.370<br>(thiophene) | 1.423<br>(thiophene) | 1.714<br>(thiophene) | 1.078<br>(thiophene) |
| $h_{sc}$ ( $a_0$ )                      | 0.63517              | 1.17792              | 0.61671              | 1.15326              |
| $e$                                     | 0.89910              | 0.74961              | 0.93513              | 0.65928              |

Table 15.281. The MO to HO intercept geometrical bond parameters of thiophene.  $R_i$  is an alkyl group and  $R, R', R''$  are H or alkyl groups.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{msp}^3, \text{AO})$ .

| Bond                            | Atom   | $E_T$<br>(eV)<br>Bond 1 | $E_T$<br>(eV)<br>Bond 2 | $E_T$<br>(eV)<br>Bond 3 | $E_T$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>$C2sp^3$<br>(eV) | $r_{\text{initial}}$<br>( $a_0$ ) | $r_{\text{final}}$<br>( $a_0$ ) | $E_{\text{bond}}(C2sp^3)$<br>(eV)<br>Final | $E(C2sp^3)$<br>(eV)<br>Final | $\theta'$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | $d_1$<br>( $a_0$ ) | $d_2$<br>( $a_0$ ) |
|---------------------------------|--------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------------------------|-----------------------------------|---------------------------------|--------------------------------------------|------------------------------|---------------------------|----------------------------|----------------------------|--------------------|--------------------|
| $C-H$ ( $C, H$ )                | $C_s$  | -1.13380                | -0.72457                | 0                       | 0                       | -153.47406                                | 0.91771                           | 0.81549                         | -16.68412                                  | -16.49326                    | 84.49                     | 95.51                      | 44.74                      | 1.08953            | 0.07833            |
| $C-H$ ( $C, H$ )                | $C'_s$ | -1.13380                | -1.13380                | 0                       | 0                       | -153.88328                                | 0.91771                           | 0.79597                         | -17.09334                                  | -16.90248                    | 82.21                     | 97.79                      | 43.14                      | 1.11914            | 0.10794            |
| $C_s = (H)C_s - C'_s(H) = C'_s$ | $C'_s$ | -1.13380                | -1.13380                | 0                       | 0                       | -153.88328                                | 0.91771                           | 0.79597                         | -17.09334                                  | -16.90248                    | 91.57                     | 88.43                      | 42.49                      | 1.31226            | 0.02177            |
| $C'_s = C_s(H)(H)C'_s = C'_s$   | $C'_s$ | -1.13380                | -1.13380                | 0                       | 0                       | -153.88328                                | 0.91771                           | 0.79597                         | -17.09334                                  | -16.90248                    | 136.36                    | 43.64                      | 59.86                      | 0.72857            | 0.57606            |
| $NC_s = C_s(H)$                 | $C'_s$ | -1.13380                | -0.72457                | 0                       | 0                       | -153.47406                                | 0.91771                           | 0.81549                         | -16.68412                                  | -16.49326                    | 137.14                    | 42.86                      | 60.85                      | 0.70685            | 0.59777            |
| $C'_s - C_s = C'_s(H)$          | $C'_s$ | -1.13380                | -0.72457                | 0                       | 0                       | -153.47406                                | 0.91771                           | 0.81549                         | -16.68412                                  | -16.49326                    | 141.52                    | 38.48                      | 55.36                      | 0.98926            | 0.63840            |
| $C'_s - C_s - C'_s = C'_s(H)$   | $S$    | -0.72457                | -0.72457                | 0                       | 0                       |                                           | 1.37001                           | 0.83600                         | -16.27490                                  |                              | 142.17                    | 37.83                      | 56.24                      | 0.96733            | 0.66033            |



Table 15.282. The energy parameters (eV) of functional groups of thiophene.

| Parameters                                     | C=C<br>Group | C-C<br>Group | C-S-C<br>Group | CH<br>Group |
|------------------------------------------------|--------------|--------------|----------------|-------------|
| $n_1$                                          | 2            | 1            | 2              | 1           |
| $n_2$                                          | 0            | 0            | 0              | 0           |
| $n_3$                                          | 0            | 0            | 0              | 0           |
| $c_1$                                          | 0.5          | 0.5          | 0.5            | 0.75        |
| $c_2$                                          | 0.85252      | 1            | 0.65700        | 1           |
| $c_3$                                          | 1            | 1            | 1              | 1           |
| $c_4$                                          | 0.85252      | 0.85252      | 0.85252        | 0.91771     |
| $c_5$                                          | 0            | 0            | 0              | 1           |
| $c_6$                                          | 4            | 2            | 4              | 1           |
| $c_7$                                          | 0            | 0            | 0              | 1           |
| $c_{10}$                                       | 0.5          | 0.5          | 0.5            | 0.75        |
| $c_{20}$                                       | 0.85252      | 1            | 0.65700        | 1           |
| $V_c$ (eV)                                     | -104.37986   | -33.80733    | -96.78916      | -39.09538   |
| $V_p$ (eV)                                     | 20.85777     | 10.19898     | 16.71820       | 13.45505    |
| $T$ (eV)                                       | 35.96751     | 9.49831      | 27.80371       | 12.74462    |
| $V_m$ (eV)                                     | -17.98376    | -4.74915     | -13.90186      | -6.37231    |
| $E_{[10,10]}$ (eV)                             | 0            | -14.63489    | 0              | -14.63489   |
| $\Delta E_{H,10}$ (eV)                         | -2.26759     | -1.85836     | -2.89830       | -2.26758    |
| $E_{T,[10,10]}$ (eV)                           | 2.26759      | -12.77653    | 2.89830        | -12.36731   |
| $E_{T,[11,10]}$ (eV)                           | -63.27075    | -31.63572    | -63.27080      | -31.63553   |
| $E_T$ (atom-atom, $\text{mmp}^3$ , $AO$ ) (eV) | -2.26759     | -2.26759     | -2.89830       | 0           |
| $E_{T,[10]}$ (eV)                              | -65.53833    | -33.90295    | -66.16903      | -31.63537   |
| $\omega$ ( $10^{15}$ rad/s)                    | 15.4421      | 12.3131      | 10.3184        | 28.9084     |
| $E_K$ (eV)                                     | 10.16428     | 8.10471      | 6.79173        | 19.02803    |
| $E_P$ (eV)                                     | -0.20668     | -0.19095     | -0.17058       | -0.27301    |
| $E_{K_{\text{orb}}}$ (eV)                      | 0.17897      | 0.14829      | 0.08146        | 0.39427     |
|                                                | [6]          | [48]         | [41]           | [56]        |
| $E_{\text{res}}$ (eV)                          | -0.11720     | -0.11680     | -0.12985       | -0.07587    |
| $E_{\text{img}}$ (eV)                          | 0.14803      | 0.14803      | 0.14803        | 0.14803     |
| $E_T$ (comp) (eV)                              | -65.77272    | -34.01976    | -66.42873      | -31.71124   |
| $E_{\text{mold}}(E_{1,10,10})$ (eV)            | -14.63489    | -14.63489    | -14.63489      | -14.63489   |
| $E_{\text{mold}}(E_{1,10,10})$ (eV)            | 0            | 0            | 0              | -13.59844   |
| $E_{T,1}$ (comp) (eV)                          | 7.23317      | 4.74998      | 7.88917        | 3.32988     |

Table 15.283. The total bond energies of thiophene calculated using the functional group composition and the energies of Table 15.282 compared to the experimental values [2].

| Name<br>Formula                           | C=C                                     |                                           | C-C               |  | C-S-C |  | CH |  |
|-------------------------------------------|-----------------------------------------|-------------------------------------------|-------------------|--|-------|--|----|--|
|                                           | Calculated<br>Total Bond<br>Energy (eV) | Experimental<br>Total Bond Energy<br>(eV) | Relative<br>Error |  |       |  |    |  |
| C <sub>4</sub> H <sub>4</sub> S Thiophene | 40.42501                                | 40.430                                    | 0.00013           |  |       |  |    |  |

Table 15.284. The bond angle parameters of thiophene and experimental values [1]. In the calculation of  $\theta_i$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(atom-atom, msp^3, AO)$ .

| Atoms of Angle     | 2c'<br>Bond 1<br>( $\theta_1$ ) | 2c'<br>Bond 2<br>( $\theta_2$ ) | 2c'<br>Terminal<br>Atoms<br>( $\theta_3$ ) | $E_{Calc}^{Calc}$<br>Atom 1 | Atom 1<br>Hybridization<br>Designation<br>(Table 15.3.B) | $E_{Calc}^{Calc}$<br>Atom 2 | Atom 2<br>Hybridization<br>Designation<br>(Table 15.3.B) | $c_2$<br>Atom 1<br>Eq.<br>(15.63) | $c_1$<br>Atom 2<br>Eq.<br>(15.126) | $C_1$ | $C_2$                      | $c_1$  | $c_2'$  | $E_T$<br>(eV) | $\theta_r$<br>(°) | $\theta_t$<br>(°) | $\theta_s$<br>(°) | Cal. $\theta$<br>(°) | Exp. $\theta$<br>(°) |
|--------------------|---------------------------------|---------------------------------|--------------------------------------------|-----------------------------|----------------------------------------------------------|-----------------------------|----------------------------------------------------------|-----------------------------------|------------------------------------|-------|----------------------------|--------|---------|---------------|-------------------|-------------------|-------------------|----------------------|----------------------|
|                    |                                 |                                 |                                            |                             |                                                          |                             |                                                          |                                   |                                    |       |                            |        |         |               |                   |                   |                   |                      |                      |
| $\angle HC_2S$     | 2.02241                         | 3.25533                         | 4.6030                                     | -15.55033                   | 3                                                        | -10.36001                   | S                                                        | 0.87495<br>Eq.<br>(15.63)         | 0.76144<br>Eq.<br>(15.126)         | 0.75  | 0.76144<br>Eq.<br>(15.126) | 0.75   | 0.87495 | 0             |                   |                   |                   | 119.58               | 119.9<br>(thiophene) |
| $\angle C_2C_2H_2$ |                                 |                                 |                                            |                             |                                                          |                             |                                                          |                                   |                                    |       |                            | 119.58 |         |               |                   | 119.58            | 115.84            | 124.58               |                      |
| $\angle HC_2C_2$   | 2.02241                         | 2.66807                         | 4.1633                                     | -16.68412                   | 14                                                       | -15.95954                   | C <sub>s</sub>                                           | 0.81549                           | 0.85252                            | 0.75  | 1                          | 0.75   | 1.04540 | 0             |                   |                   |                   | 124.58               | 124.3<br>(thiophene) |
| $\angle HC_2C_2$   | 2.02241                         | 2.60925                         | 4.1633                                     | -16.68412                   | 14                                                       | -15.95954                   | C <sub>s</sub>                                           | 0.81549                           | 0.85252                            | 0.75  | 1                          | 0.75   | 1.04540 | 0             |                   |                   |                   | 127.57               |                      |
| $\angle HC_2C_2$   | 2.02241                         | 2.60925                         | 4.0825                                     | -17.09334                   | 18                                                       | -16.68412                   | C <sub>s</sub>                                           | 0.79597                           | 0.81549                            | 0.75  | 1                          | 0.75   | 1.02453 | 0             |                   |                   |                   | 123.13               |                      |
| $\angle C_2C_2H_2$ |                                 |                                 |                                            |                             |                                                          |                             |                                                          |                                   |                                    |       |                            |        |         |               |                   | 123.13            | 113.60            | 123.27               | 124.3<br>(thiophene) |
| $\angle C_2C_2S$   | 2.60925                         | 3.25533                         | 4.9809                                     | -17.81791                   | 27                                                       | -10.36001                   | S                                                        | 0.76360<br>Eq.<br>(15.153)        | 0.65700<br>Eq.<br>(15.153)         | 1     | 0.65700<br>Eq.<br>(15.153) | 1      | 0.71030 | -0.72457      |                   |                   |                   | 115.84               | 115.5<br>(thiophene) |
| $\angle C_2SC_2$   | 3.25533                         | 3.25533                         | 4.7958                                     | -16.68412                   | 14                                                       | -16.68412                   | C <sub>s</sub>                                           | 0.81549                           | 0.81549                            | 1     | 1                          | 1      | 0.81549 | -1.85836      |                   |                   |                   | 94.89                | 92.2<br>(thiophene)  |
| $\angle C_2C_2C_2$ | 2.60925                         | 2.66807                         | 4.4159                                     | -16.88873                   | 15                                                       | -18.02252                   | 29                                                       | 0.80561                           | 0.75493                            | 1     | 1                          | 1      | 0.78027 | -1.85836      |                   |                   |                   | 113.60               | 112.5<br>(thiophene) |

## IMIDAZOLE

Imidazole having the formula  $C_3H_4N_2$  comprises a conjugated system that is equivalent to pyrrole with one of the conjugated  $CH$  groups replaced by a nitrogen atom. The  $CH$ ,  $NH$ , and  $C=C$  groups are equivalent to the corresponding groups of pyrrole, 5 furan, and thiophene where present. In addition, the nitrogen substitution creates a  $C-N=C$  moiety comprising  $C-N$  and  $N=C$  functional groups. The  $C-N$  bonding is the same as that of a tertiary amine except that the hybridization term  $c_2$  in Eqs. (15.42) and (15.52) is that of the amino group of aniline,  $c_2(arylC2sp^3HO\ to\ N)=0.84665$  (Eq. (15.152)). The hybridization factor provides double-bond character to match the group to the 10 other orbitals of the molecule.  $\Delta E_{H_2MO}(AO/HO)$  in Eq. (15.42) and  $E_T(atom-atom,msp^3.AO)$  in Eq. (15.52) are both  $-0.92918\ eV$  (Eq. (14.513)). This matches the energy of the group to that of the contiguous  $N=C$  group wherein  $\Delta E_{H_2MO}(AO/HO)$  in Eq. (15.42) and  $E_T(atom-atom,msp^3.AO)$  in Eq. (15.52) are both  $-0.92918\ eV$  (Eq. (14.513)) per atom of the double bond with aromatic character as in the 15 case of the prior heterocyclic compounds. As in the prior cases of pyrrole, furan, and thiophene,  $n_1=2$  and  $C_2$  and  $C_{2v}$  are the same as  $C_2(benzeneC2sp^3HO)=0.85252$  (Eq. (15.143)) in Eqs. (15.42) and (15.52). To match the energy of the nitrogen to the  $C2sp^3\ HO$ ,  $c_2$  of the  $N=C$ -bond MO is also given by Eq. (15.152). These parameters also provide an energy match to the  $C-N-C$  group.

20 As in the case of pyrrole, the  $C-N-C$ -bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with  $n_1=2$  in Eqs. (15.42) and (15.52). The hybridization factor  $c_2(arylC2sp^3HO\ to\ N)=0.84665$  (Eq. (15.152)) matches the double-bond character of the  $C2sp^3\ HOs$  to the  $N$  atom of the  $NH$  group, and  $C_2$  and  $C_{2v}$  in Eqs. (15.42) and (15.52) become that of benzene given by Eq. 25 (15.143),  $C_2(benzeneC2sp^3HO)=0.85252$ . Furthermore,  $\Delta E_{H_2MO}(AO/HO)$  in Eq. (15.42) and  $E_T(atom-atom,msp^3.AO)$  in Eq. (15.52) are both  $-0.92918\ eV$  (Eq. (14.513)) per atom corresponding to  $-3.71673\ eV$  in total.

The symbols of the functional groups of imidazole are given in Table 15.285. The structure of imidazole is shown in Figure 68. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of imidazole are given in Tables 15.286, 15.287, and 15.288, respectively. The total energy of imidazole given in Table 15.289 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.288 corresponding to functional-group composition of the molecule. The bond angle parameters of imidazole determined using Eqs. (15.79-15.108) are given in Table 15.290.

10 Table 15.285. The symbols of functional groups of imidazole.

| Functional Group        | Group Symbol |
|-------------------------|--------------|
| $C_a = C_b$ double bond | $C = C$      |
| $N_b = C_c$ double bond | $N = C$      |
| $C_b - N_b$             | $C - N$      |
| $C_a - N_a - C_c$       | $C - N - C$  |
| $N_a H$ group           | $NH$         |
| CH                      | $CH$         |

Table 15.286. The geometrical bond parameters of imidazole and experimental values [1].

| Parameter                               | C=C<br>Group       | N=C<br>Group | C-N<br>Group | C-N-C<br>Group     | NH<br>Group        | CH<br>Group        |
|-----------------------------------------|--------------------|--------------|--------------|--------------------|--------------------|--------------------|
| $a$ ( $a_0$ )                           | 1.45103            | 1.44926      | 1.82450      | 1.43222            | 1.24428            | 1.53380            |
| $c'$ ( $a_0$ )                          | 1.30463            | 1.30383      | 1.35074      | 1.29614            | 0.94134            | 1.01120            |
| Bond Length<br>$2c'$ ( $\text{\AA}$ )   | 1.38076            | 1.37991      | 1.42956      | 1.37178            | 0.996270           | 1.07021            |
| Exp. Bond<br>Length<br>( $\text{\AA}$ ) | 1.382<br>(pyrrole) |              |              | 1.370<br>(pyrrole) | 0.996<br>(pyrrole) | 1.076<br>(pyrrole) |
| $h, c$ ( $a_0$ )                        | 0.63517            | 0.63276      | 1.22650      | 0.60931            | 0.81370            | 1.15326            |
| $e$                                     | 0.89910            | 0.89965      | 0.74033      | 0.90499            | 0.75653            | 0.65928            |

Table 15.287. The MO to HO intercept geometrical bond parameters of imidazole.  $R_i$  is an alkyl group and  $R, R', R''$  are H or alkyl groups.  $E_i$  is  $E_i(\text{atom} - \text{atom}, \text{insp}^3, \text{AO})$ .

| Bond                           | Atom   | $E_r$<br>(eV)<br>Bond 1 | $E_r$<br>(eV)<br>Bond 2 | $E_r$<br>(eV)<br>Bond 3 | $E_r$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>$C'2sp^3$<br>(eV) | $r_{\text{bond}}$<br>( $a_0$ ) | $E_{\text{bond}}$<br>(eV)<br>Final | $E(C'2sp^3)$<br>(eV)<br>Final | $\theta'$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | $d_1$<br>( $a_0$ ) | $d_2$<br>( $a_0$ ) |
|--------------------------------|--------|-------------------------|-------------------------|-------------------------|-------------------------|--------------------------------------------|--------------------------------|------------------------------------|-------------------------------|---------------------------|----------------------------|----------------------------|--------------------|--------------------|
| $C'-H$ ( $C', H$ )             | $C'_a$ | -1.13380                | -0.92918                | 0                       | 0                       | -153.67867                                 | 0.91771                        | -16.88873                          | -16.69786                     | 83.35                     | 96.65                      | 43.94                      | 1.10452            | 0.08931            |
| $C'-H$ ( $C', H$ )             | $C'_b$ | -1.13380                | -0.46459                | 0                       | 0                       | -153.21408                                 | 0.91771                        | -16.42414                          | -16.23327                     | 85.93                     | 94.07                      | 45.77                      | 1.06995            | 0.03875            |
| $C'-H$ ( $C', H$ )             | $C'_c$ | -0.92918                | -0.92918                | 0                       | 0                       | -153.47605                                 | 0.91771                        | -16.68411                          | -16.49325                     | 84.49                     | 95.51                      | 44.47                      | 1.08953            | 0.07833            |
| $C'_a = (H)C'_b - N'_a = C'_c$ | $C'_b$ | -0.46459                | -1.13380                | 0                       | 0                       | -153.21408                                 | 0.91771                        | -16.42414                          | -16.23327                     | 90.36                     | 89.64                      | 42.49                      | 1.34547            | 0.00527            |
| $C'_a = (H)C'_b - N'_a = C'_c$ | $N'_a$ | -0.46459                | -0.92918                | 0                       | 0                       |                                            | 0.93084                        |                                    |                               | 91.32                     | 88.68                      | 43.14                      | 1.31135            | 0.01939            |
| $C'_a = (H)N'_a = C'_c$        | $C'_a$ | -1.13380                | -0.46459                | 0                       | 0                       | -153.21408                                 | 0.91771                        | -16.42414                          | -16.23327                     | 137.64                    | 42.36                      | 61.49                      | 0.69250            | 0.61213            |
| $HN'_aC'_a = C'_b(H)$          | $C'_c$ | -1.13380                | -0.92918                | 0                       | 0                       | -153.67867                                 | 0.91771                        | -16.88873                          | -16.69786                     | 136.75                    | 43.25                      | 60.35                      | 0.71784            | 0.58678            |
| $C'_b(H)N'_a - C'_a = C'_b(H)$ | $C'_c$ | -0.92918                | -0.92918                | 0                       | 0                       |                                            | 0.91771                        |                                    |                               | 138.54                    | 41.46                      | 61.09                      | 0.69238            | 0.60376            |
| $C'_b(H)N'_a - C'_a = C'_b(H)$ | $N'_a$ | -0.92918                | -0.92918                | 0                       | 0                       |                                            | 0.91771                        | -16.88873                          | -16.69786                     | 138.92                    | 41.08                      | 61.59                      | 0.68147            | 0.61467            |
| $N'_a - H$ ( $N'_a, H$ )       | $N'_a$ | -0.92918                | -0.92918                | 0                       | 0                       |                                            | 0.93084                        | -16.68411                          |                               | 117.34                    | 62.66                      | 62.90                      | 0.36678            | 0.37456            |
| $(H)C'_c - N'_aC'_a = C'_b(H)$ | $C'_c$ | -0.92918                | -0.92918                | 0                       | 0                       | -153.47605                                 | 0.91771                        | -16.68411                          | -16.49325                     | 138.92                    | 41.08                      | 61.59                      | 0.68147            | 0.61467            |
| $C'_a = (H)C'_bN'_a = C'_c$    | $C'_c$ | -0.92918                | -0.92918                | 0                       | 0                       | -153.47605                                 | 0.91771                        | -16.68411                          | -16.49325                     | 137.31                    | 42.69                      | 60.92                      | 0.70446            | 0.59938            |
| $C'_a = (H)C'_bN'_a = C'_c$    | $N'_a$ | -0.92918                | -0.46459                | 0                       | 0                       |                                            | 0.93084                        | -16.21953                          |                               | 138.20                    | 41.80                      | 62.08                      | 0.67849            | 0.62534            |

Table 15.288. The energy parameters (eV) of functional groups of imidazole.

| Parameters                | C=C<br>Group | N=C<br>Group | C-N<br>Group | C-N-C<br>Group | NH<br>Group | CH<br>Group |
|---------------------------|--------------|--------------|--------------|----------------|-------------|-------------|
| $\eta_1$                  | 2            | 2            | 1            | 2              | 1           | 1           |
| $\eta_2$                  | 0            | 0            | 0            | 0              | 0           | 0           |
| $\eta_3$                  | 0            | 0            | 0            | 0              | 0           | 0           |
| $C_1$                     | 0.5          | 0.5          | 0.5          | 0.5            | 0.75        | 0.75        |
| $C_2$                     | 0.85252      | 0.85252      | 1            | 0.85252        | 0.93613     | 1           |
| $C_3$                     | 1            | 1            | 1            | 1              | 0.75        | 1           |
| $C_4$                     | 0.85252      | 0.84665      | 0.84665      | 0.84665        | 0.92171     | 0.91771     |
| $C_5$                     | 0            | 0            | 0            | 0              | 1           | 1           |
| $C_6$                     | 4            | 4            | 2            | 4              | 1           | 1           |
| $C_7$                     | 0            | 0            | 0            | 0              | 1           | 1           |
| $C_8$                     | 0.5          | 0.5          | 0.5          | 0.5            | 0.75        | 0.75        |
| $C_{10}$                  | 0.85252      | 0.85252      | 1            | 0.85252        | 1           | 1           |
| $V_2$ (eV)                | -104.37986   | -103.92756   | -32.44864    | -106.58684     | -39.48897   | -39.09538   |
| $V_3$ (eV)                | 20.85777     | 20.87050     | 10.07285     | 20.99432       | 14.45367    | 13.45505    |
| $T$ (eV)                  | 35.96751     | 35.85539     | 8.89248      | 37.21047       | 15.86820    | 12.74462    |
| $V_4$ (eV)                | -17.98376    | -17.92770    | -4.44624     | -18.60523      | -7.93410    | -6.37231    |
| $E_1$ (eV)                | 0            | 0            | -14.63489    | 0              | -14.53414   | -14.63489   |
| $\Delta E_{H_{1,2}}$ (eV) | -2.26759     | -1.85836     | -0.92918     | -3.71673       | 0           | -2.26758    |
| $E_2$ (eV)                | 2.26759      | 1.85836      | -13.70571    | 3.71673        | -14.53414   | -12.36731   |
| $E_3$ (eV)                | -63.27075    | -63.27100    | -31.63527    | -63.27056      | -31.63534   | -31.63533   |
| $E_4$ (eV)                | -2.26759     | -1.85836     | -0.92918     | -3.71673       | 0           | 0           |
| $E_5$ (eV)                | -65.53833    | -65.12910    | -32.56455    | -66.98746      | -31.63537   | -31.63537   |
| $\omega$ ( $10^6$ rad/s)  | 15.4421      | 15.4704      | 21.5213      | 15.7474        | 48.7771     | 28.9084     |
| $E_6$ (eV)                | 10.16428     | 10.18290     | 14.16571     | 10.36521       | 32.10594    | 19.02803    |
| $E_7$ (eV)                | -0.20668     | -0.20558     | -0.24248     | -0.21333       | -0.35462    | -0.27301    |
| $E_8$ (eV)                | 0.17897      | 0.20768      | 0.12944      | 0.11159        | 0.40696     | 0.39427     |
| $E_9$ (eV)                | -0.11720     | -0.10174     | -0.17775     | -0.15754       | -0.15115    | -0.07587    |
| $E_{10}$ (eV)             | 0.14803      | 0.14803      | 0.14803      | 0.14803        | 0.14803     | 0.14803     |
| $E_{11}$ (eV)             | -65.77272    | -65.33259    | -32.74230    | -67.30254      | -31.78651   | -31.71124   |
| $E_{12}$ (eV)             | -14.63489    | -14.63489    | -14.63489    | -14.63489      | -14.53414   | -14.63489   |
| $E_{13}$ (eV)             | 0            | 0            | 0            | 0              | -13.59844   | -13.59844   |
| $E_{14}$ (eV)             | 7.23317      | 6.79303      | 3.47253      | 8.76298        | 3.51208     | 3.32988     |

Table 15.289. The total bond energies of imidazole calculated using the functional group composition and the energies of Table 15.288 compared to the experimental values [2].

| Formula     | Name      | $C=C$ | $N=C$ | $C-N$ | $C-N-C$ | NH | CH | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|-------------|-----------|-------|-------|-------|---------|----|----|-----------------------------------|-------------------------------------|----------------|
| $C_4H_4N_2$ | Imidazole | 1     | 1     | 1     | 1       | 1  | 3  | 39.74106                          | 39.74106                            | -0.00056       |

Table 15.290. The bond angle parameters of imidazole and experimental values [59]. In the calculation of  $\theta_{\alpha}$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(atom - atom, nsp, AO)$ .

| Atom of Angle      | $2c_1^*$ Bond 1 ( $\alpha_1$ ) | $2c_2^*$ Bond 2 ( $\alpha_2$ ) | $2c_3^*$ Terminal Atoms ( $\alpha_3$ ) | $E_{\text{calculated}}$ Atom 1 | Atom 1 Hybridization Designation (Table 15.3B) | $E_{\text{calculated}}$ Atom 2 | Atom 2 Hybridization Designation (Table 15.3B) | $c_2$ Atom 1                 | $c_3$ Atom 2                 | $C_1$ | $C_2$ | $-c_1$ | $c_2^*$ | $E_r$ (eV) | $\theta_r$ ( $^\circ$ ) | $\theta_1$ ( $^\circ$ ) | $\theta_2$ ( $^\circ$ ) | Cal. $\theta$ ( $^\circ$ ) | Exp. $\theta$ ( $^\circ$ ) |
|--------------------|--------------------------------|--------------------------------|----------------------------------------|--------------------------------|------------------------------------------------|--------------------------------|------------------------------------------------|------------------------------|------------------------------|-------|-------|--------|---------|------------|-------------------------|-------------------------|-------------------------|----------------------------|----------------------------|
| $\angle HC_1N_a$   | 2.02341                        | 2.59228                        | 4.0166                                 | -14.82575                      | I                                              | -14.53414                      | N                                              | 0.91771                      | 0.92171<br>(Eq.<br>(15.151)) | 0.75  | I     | 0.75   | 1.00435 | 0          |                         |                         |                         | 120.51                     | 117.4<br>(midazole)        |
| $\angle C_2C_3H_a$ |                                |                                |                                        |                                |                                                |                                |                                                |                              |                              |       |       |        |         |            |                         | 120.51                  | 106.63                  | 132.86                     | 136.3<br>(midazole)        |
| $\angle HN_1C_a$   | 1.88268                        | 2.59228                        | 3.8987                                 | -14.53414                      | N                                              | -16.49325                      | I3                                             | 0.84665<br>(Eq.<br>(15.151)) | 0.82493<br>(Eq.<br>(15.64))  | 0.75  | I     | 0.75   | 0.97035 | 0          |                         |                         |                         | 120.37                     | 122.9<br>(midazole)        |
| $\angle H_1C_1C_a$ | 2.02341                        | 2.60925                        | 4.2895                                 | -16.88873                      | 15                                             | -15.72493                      | $C_1$                                          | 0.80561                      | 0.86359                      | 0.75  | I     | 0.75   | 1.07196 | 0          |                         |                         |                         | 135.30                     | 136.3<br>(midazole)        |
| $\angle H_1C_1C_a$ | 2.02341                        | 2.60925                        | 4.2740                                 | -15.95954                      | 6                                              | -14.82575                      | $C_2$                                          | 0.83252                      | 0.91771                      | 0.75  | I     | 0.75   | 1.07647 | 0          |                         |                         |                         | 134.28                     | 133.2<br>(midazole)        |
| $\angle N_1C_1H_b$ |                                |                                |                                        |                                |                                                |                                |                                                |                              |                              |       |       |        |         |            |                         | 134.28                  | 111.18                  | 114.54                     | 115.8<br>(midazole)        |
| $\angle H_1C_1N_a$ | 2.02341                        | 2.59228                        | 3.8471                                 | -15.95954                      | 6                                              | -14.53414                      | N                                              | 0.87495                      | 0.84665<br>(Eq.<br>(15.152)) | 0.75  | I     | 0.75   | 0.96765 |            |                         |                         |                         | 112.37                     | 110.4<br>(midazole)        |
| $\angle N_1C_1H_c$ |                                |                                |                                        |                                |                                                |                                |                                                |                              |                              |       |       |        |         |            |                         | 112.37                  | 109.83                  | 137.80                     | 138.2<br>(midazole)        |
| $\angle HN_1C_2$   | 1.88268                        | 2.59228                        | 4.0661                                 | -14.53414                      | N                                              | -15.76868                      | 6                                              | 0.84665<br>(Eq.<br>(15.151)) | 0.86284<br>(Eq.<br>(15.64))  | 0.75  | I     | 0.75   | 1.01912 | 0          |                         |                         |                         | 129.96                     | 129.1<br>(midazole)        |
| $\angle N_1C_1C_a$ | 2.59228                        | 2.60925                        | 4.1952                                 | -14.53414                      | N                                              | -17.09334                      | 18                                             | 0.84665<br>(Eq.<br>(15.152)) | 0.79597                      | I     | I     | I      | 0.82131 | -1.44915   |                         |                         |                         | 107.52                     | 106.3<br>(midazole)        |
| $\angle C_2N_1C_2$ | 2.59228                        | 2.59228                        | 4.2426                                 | -17.81791                      | 26                                             | -17.81791                      | 26                                             | 0.76360                      | 0.76360                      | I     | I     | I      | 0.76360 | -1.85836   |                         |                         |                         | 109.83                     | 107.2<br>(midazole)        |
| $\angle C_1C_1C_a$ | 2.60766                        | 2.70148                        | 4.3128                                 | -17.61330                      | 23                                             | -17.61330                      | 25                                             | 0.77247                      | 0.77247                      | I     | I     | I      | 0.77247 | -1.85836   |                         |                         |                         | 108.64                     | 105.4<br>(midazole)        |
| $\angle C_1C_1N_b$ | 2.60925                        | 2.70148                        | 4.3818                                 | -15.95955                      | 6                                              | -14.53414                      | N                                              | 0.85252                      | 0.84665<br>(Eq.<br>(15.152)) | I     | I     | I      | 0.84958 | -1.85836   |                         |                         |                         | 111.18                     | 109.8<br>(midazole)        |
| $\angle N_1C_1N_b$ | 2.59228                        | 2.60766                        | 4.2544                                 | -16.68411                      | 13                                             | -16.21953                      | 8                                              | 0.81549                      | 0.83885                      | I     | I     | I      | 0.82717 | -1.44915   |                         |                         |                         | 109.80                     | 111.3<br>(midazole)        |

## PYRIDINE

Pyridine has the formula  $C_5H_5N$  and comprises the benzene molecule with one  $CH$  group replaced by a nitrogen atom which gives rise to a  $C=N$  functional group. The aromatic  $C=C$  and  $C-H$  functional groups are equivalent to those of benzene given in the 5 Aromatic and Heterocyclic Compounds section with the aromaticity maintained by the electrons from nitrogen in the  $C=N$  group which is also aromatic.

As in the case of the aromatic carbons of benzene, each pyridine  $C2sp^3$  HO initially has four unpaired electrons. Each  $C-H$  bond has two paired electrons with one donated from the  $H$  AO and the other from the  $C2sp^3$  HO. In pyridine the three  $N2p$  electrons are 10 donated to the aromatic bond. Thus, as in the case of the  $C=C$  group, each  $C=N$  bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from the  $C2sp^3$  HO and the  $N2p$  AO of the participating carbon and nitrogen atoms, respectively.

The solution of the  $C=N$  functional group comprises the hybridization of the  $2s$  and 15  $2p$  AOs of each  $C$  to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the nitrogen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. The  $C=N$ -bond MO is solved as a double bond with  $n_1 = 2$  in Eqs. (15.42) and (15.147). The hybridization factor  $c_2(C2sp^3HO \text{ to } N) = 0.91140$  (Eq. (15.116)) matches the double-bond character of the 20  $C2sp^3$  HO to the  $N$  atom, and  $C_2$  and  $C_{2o}$  in Eqs. (15.42) and (15.147) are also given by Eq. (15.116) in order to match the nitrogen to the aromatic  $C2sp^3$  HO such that  $\Delta E_{H_2MO}(AO/HO) = 0$  in Eq. (15.42). Furthermore,  $E_r(atom - atom, msp^3.AO)$  of the  $C=N$ -bond MO in Eq. (15.147) due to the charge donation from the  $C$  and  $N$  atoms to the MO is  $-1.44915 \text{ eV}$  corresponding to an energy contribution from each atom that is 25 equivalent to that of an independent methyl group,  $-0.72457 \text{ eV}$  (Eq. (14.151)). The contributions are also the same as those for a primary amine group as given in the corresponding section. As in the case of benzene, the aromatic  $E_r(Group)$  and  $E_D(Group)$  are



given by Eqs. (15.146) and (15.147), respectively, with  $f_1 = 0.75$ . The breakage of the *CNC* bonds results in three unpaired electrons on the *N* atom. Thus, the corresponding  $E_{mag}$  given by Eq. (15.60) was normalized for the two bonds per atom and for  $f_1 = 0.75$  and was subtracted from the total energy of the  $C \overset{3e}{=} N$ -bond MO in Eq. (15.147). The pyridine vibrational energies are similar to those of benzene [60]; thus, the value for benzene was used.

The symbols of the functional groups of pyridine are given in Table 15.291. The corresponding designation of the structure is shown in Figure 69. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of pyridine are given in Tables 15.292, 15.293, and 15.294, respectively. The total energy of pyridine given in Table 15.295 was calculated as the sum over the integer multiple of each  $E_D(\text{group})$  of Table 15.294 corresponding to functional-group composition of the molecule. The bond angle parameters of pyridine determined using Eqs. (15.79-15.108) are given in Table 15.296.

Table 15.291. The symbols of functional groups of pyridine.

| Functional Group        | Group Symbol          |
|-------------------------|-----------------------|
| CC (aromatic bond)      | $C \overset{3e}{=} C$ |
| CH (aromatic)           | $CH$                  |
| $C_a \overset{3e}{=} N$ | $C \overset{3e}{=} N$ |

Table 15.292. The geometrical bond parameters of pyridine and experimental values [1].

| Parameter            | C=C Group        | C-H Group        | C=N Group        |
|----------------------|------------------|------------------|------------------|
| $a(a_0)$             | 1.47348          | 1.60061          | 1.47169          |
| $c'(a_0)$            | 1.31468          | 1.03299          | 1.27073          |
| Bond Length $2c'(A)$ | 1.39140          | 1.09327          | 1.34489          |
| Exp. Bond Length (A) | 1.394 (pyridine) | 1.084 (pyridine) | 1.340 (pyridine) |
| $b_0c'(a_0)$         | 0.66540          | 1.22265          | 0.74237          |
| $e$                  | 0.89223          | 0.64537          | 0.86345          |

Table 15.293. The MO to HOMO intercept geometrical bond parameters of pyridine.  $E_T$  is  $E_T(atom-atom, msp, AO)$ .

| Bond                     | Atom   | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C'2sp^3$ (eV) | $r_{final}$ ( $a_0$ ) | $E_{total}(C'2sp^3)$ (eV) Final | $\bar{E}(C'2sp^3)$ (eV) Final | $\theta^*$ (°) | $\theta_1$ (°) | $\theta_2$ (°) | $d_1$ ( $a_0$ ) | $d_2$ ( $a_0$ ) |
|--------------------------|--------|-------------------|-------------------|-------------------|-------------------|-----------------------------------|-----------------------|---------------------------------|-------------------------------|----------------|----------------|----------------|-----------------|-----------------|
| $C-H(C'H)$               | $C'$   | -0.54343          | -0.85035          | -0.56690          | 0                 | -153.57636                        | 0.91771               | -16.78642                       | -16.59556                     | 76.35          | 103.65         | 40.11          | 1.22423         | 0.19124         |
| $C-H(C'H)$               | $C'$   | -0.85035          | -0.85035          | -0.56690          | 0                 | -153.88327                        | 0.91771               | -17.09334                       | -16.90248                     | 74.42          | 105.58         | 38.84          | 1.24678         | 0.21379         |
| $\{H\}C'_s(H)C'_s=NC'_s$ | $C'_s$ | -0.85035          | -0.54343          | -0.56690          | 0                 | -153.57636                        | 0.91771               | -16.78642                       | -16.59556                     | 128.54         | 51.46          | 58.65          | 0.76572         | 0.50501         |
| $\{H\}C'_s(H)C'_s=NC'_s$ | $N$    | -0.54343          | -0.54343          | 0                 | 0                 |                                   | 0.93084               | -15.91261                       |                               | 130.61         | 49.39          | 60.97          | 0.71418         | 0.55656         |
| $\{H\}C'_s=NC'_s(H)N$    | $C'_s$ | -0.54343          | -0.85035          | -0.56690          | 0                 | -153.57636                        | 0.91771               | -16.78642                       | -16.59556                     | 134.85         | 45.15          | 59.72          | 0.74304         | 0.57165         |
| $\{H\}C'_s=NC'_s(H)N$    | $C'_s$ | -0.85035          | -0.85035          | -0.56690          | 0                 | -153.88327                        | 0.91771               | -17.09334                       | -16.90248                     | 134.24         | 45.76          | 58.98          | 0.75915         | 0.55533         |

Table 15.294. The energy parameters (eV) of functional groups of pyridine.

| Parameters                | C=C<br>Group | C-H<br>Group | C=N<br>Group |
|---------------------------|--------------|--------------|--------------|
| $f_1$                     | 0.75         | 1            | 0.75         |
| $n_1$                     | 2            | 1            | 2            |
| $n_2$                     | 0            | 0            | 0            |
| $n_3$                     | 0            | 0            | 0            |
| $c_1$                     | 0.5          | 0.75         | 0.5          |
| $c_2$                     | 0.85252      | 1            | 0.91140      |
| $c_3$                     | 1            | 1            | 1            |
| $c_4$                     | 0.85252      | 0.91771      | 0.91140      |
| $c_5$                     | 0            | 1            | 0            |
| $c_6$                     | 3            | 1            | 3            |
| $c_7$                     | 0            | 1            | 0            |
| $c_8$                     | 0.5          | 0.75         | 0.5          |
| $c_9$                     | 0.85252      | 1            | 0.91140      |
| $V_1$ (eV)                | -101.12679   | -37.10024    | -102.01431   |
| $V_2$ (eV)                | 20.69825     | 13.17125     | 21.41410     |
| $T$ (eV)                  | 34.31559     | 11.58941     | 34.65890     |
| $V_m$ (eV)                | -17.15779    | -5.79470     | -17.32945    |
| $E_1$ (eV)                | 0            | -14.63489    | 0            |
| $\Delta E_{1,2,3,4}$ (eV) | 0            | -1.13379     | 0            |
| $E_2$ (eV)                | 0            | -13.50110    | 0            |
| $E_3$ (eV)                | -63.27075    | -31.63539    | -63.27076    |
| $E_4$ (eV)                | -2.26759     | -0.56690     | -1.44915     |
| $E_5$ (eV)                | -65.53833    | -32.20226    | -64.71988    |
| $\omega$ ( $10^5$ rad/s)  | 49.7272      | 26.4826      | 43.6311      |
| $E_6$ (eV)                | 32.73133     | 17.43132     | 28.71875     |
| $E_7$ (eV)                | -0.35806     | -0.26130     | -0.33540     |
| $E_8$ (eV)                | 0.19649      | 0.35532      | 0.19649      |
| $E_9$ (eV)                | [49]         | Eq. (13.458) | [49]         |
| $E_{10}$ (eV)             | -0.25982     | -0.08364     | -0.23715     |
| $E_{11}$ (eV)             | 0.14803      | 0.14803      | 0.09457      |
| $E_{12}$ (eV)             | -49.54347    | -32.28590    | -48.82472    |
| $E_{13}$ (eV)             | -14.63489    | -14.63489    | -14.63489    |
| $E_{14}$ (eV)             | 0            | -13.59844    | 0            |
| $E_{15}$ (eV)             | 5.63881      | 3.90454      | 4.92005      |

Table 15.295. The total bond energies of pyridine calculated using the functional group composition and the energies of Table 15.294 compared to the experimental values [2].

| Formula   | Name     | $C \equiv C$ | $C^{\equiv}H$ | $C=N$ | Group | Calculated<br>Total Bond Energy<br>(eV) | Experimental<br>Total Bond Energy<br>(eV) | Relative Error |
|-----------|----------|--------------|---------------|-------|-------|-----------------------------------------|-------------------------------------------|----------------|
| $C_5H_5N$ | Pyridine | 4            | 5             | 2     |       | 51.91802                                | 51.87927                                  | -0.00075       |

Table 15.296. The bond angle parameters of pyridine and experimental values [1].  $E_T$  is  $E_T(atom - atom, msp, AO)$ .

| Atoms of Angle                  | $2c'$<br>Bond 1<br>( $a_s$ ) | $2c'$<br>Bond 2<br>( $a_s$ ) | $2c'$<br>Terminal<br>Atoms<br>( $a_s$ ) | $F_{Coulombic}$<br>Atom 1 | Atom 1<br>Hybridization<br>Designation<br>(Table 15.3B) | $F_{Coulombic}$<br>Atom 2 | Atom 2<br>Hybridization<br>Designation<br>(Table 15.3B) | $c_2$<br>Atom 1            | $c_2$<br>Atom 2           | $C_1$ | $C_2$ | $c_1$ | $c_2'$  | $E_T$<br>(eV) | $\theta_v$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | Cal. $\theta$<br>( $^\circ$ ) | Exp. $\theta$<br>( $^\circ$ )                                          |
|---------------------------------|------------------------------|------------------------------|-----------------------------------------|---------------------------|---------------------------------------------------------|---------------------------|---------------------------------------------------------|----------------------------|---------------------------|-------|-------|-------|---------|---------------|----------------------------|----------------------------|----------------------------|-------------------------------|------------------------------------------------------------------------|
| $\angle C' C' C'$<br>(aromatic) | 2.6936                       | 2.6936                       | 4.5585                                  | -17.17218                 | 20                                                      | -17.17218                 | 20                                                      | 0.79232                    | 0.79232                   | 1     | 1     | 1     | 0.79232 | -1.85836      |                            |                            |                            | 120.19                        | 120 [50-52]<br>(benzene)<br>118.3<br>(pyridine)<br>118.5<br>(pyridine) |
| $\angle C' C' H$<br>(aromatic)  |                              |                              |                                         |                           |                                                         |                           |                                                         |                            |                           |       |       |       |         |               |                            |                            |                            | 119.91                        | 120 [50-52]<br>(benzene)<br>121.3<br>(pyridine)                        |
| $\angle H C' N$                 | 2.06598                      | 2.54147                      | 3.9497                                  | -14.82575                 | 1                                                       | -14.53414                 | N                                                       | 0.91771<br>Eq.<br>(15.116) | 0.9140<br>Eq.<br>(15.116) | 0.75  | 1     | 0.75  | 0.99312 | 0             |                            |                            |                            | 117.65                        | 115.9<br>(pyridine)                                                    |
| $\angle N C' C'_s$              | 2.54147                      | 2.6936                       | 4.5607                                  | -14.53414                 | N                                                       | -16.52644<br>$C'_s$       | 12                                                      | 0.9140<br>Eq.<br>(15.116)  | 0.82327                   | 1     | 1     | 1     | 0.86734 | -1.44915      |                            |                            |                            | 123.76                        | 123.9<br>(pyridine)                                                    |
| $\angle C' N C'_s$              | 2.54147                      | 2.54147                      | 4.3359                                  | -17.71560                 | 24                                                      | -17.71560                 | 24                                                      | 0.76801                    | 0.76801                   | 1     | 1     | 1     | 0.76801 | -1.85836      |                            |                            |                            | 117.09                        | 116.8<br>(pyridine)                                                    |

## PYRIMIDINE

Pyrimidine has the formula  $C_4H_4N_2$  and comprises the pyridine molecule with one additional  $CH$  group replaced by a nitrogen atom which gives rise to a second  $C^{3e}=N$  functional group that is equivalent to that of pyridine given in the corresponding section. The aromatic  $C^{3e}=C$  and  $C-H$  functional groups are also equivalent to those of pyridine and benzene given in the Aromatic and Heterocyclic Compounds section with the aromaticity maintained by the electrons from nitrogen in the  $C^{3e}=N$  group which is also aromatic.

The symbols of the functional groups of pyrimidine are given in Table 15.297. The corresponding designation of the structure is shown in Figure 70. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of pyrimidine are given in Tables 15.298, 15.299, and 15.300, respectively. The total energy of pyrimidine given in Table 15.301 was calculated as the sum over the integer multiple of each  $E_D(\text{group})$  of Table 15.300 corresponding to functional-group composition of the molecule. The bond angle parameters of pyrimidine determined using Eqs. (15.79-15.108) are given in Table 15.302.

Table 15.297. The symbols of functional groups of pyrimidine.

| Functional Group     | Group Symbol |
|----------------------|--------------|
| $CC$ (aromatic bond) | $C^{3e}=C$   |
| $CH$ (aromatic)      | $CH$         |
| $C_{a,b,a}^{3e}=N$   | $C^{3e}=N$   |

Table 15.298. The geometrical bond parameters of pyrimidine and experimental values [1].

| Parameter                            | $C=C$<br>Group        | $CH$<br>Group       | $C=N$<br>Group        |
|--------------------------------------|-----------------------|---------------------|-----------------------|
| $a$ ( $a_0$ )                        | 1.47348               | 1.60061             | 1.47169               |
| $c'$ ( $a_0$ )                       | 1.31468               | 1.03299             | 1.27073               |
| Bond Length $2c'$ ( $\text{\AA}$ )   | 1.39140               | 1.09327             | 1.34489               |
| Exp. Bond Length<br>( $\text{\AA}$ ) | 1.393<br>(pyrimidine) | 1.084<br>(pyridine) | 1.340<br>(pyrimidine) |
| $b, c$ ( $a_0$ )                     | 0.66540               | 1.22265             | 0.74237               |
| $e$                                  | 0.89223               | 0.64537             | 0.86345               |

Table 15.299. The MO to HO intercept geometrical bond parameters of pyrimidine.  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{msp}^2, \text{AO})$ .

| Bond                                           | Atom           | $E_r$<br>(eV)<br>Bond 1 | $E_r$<br>(eV)<br>Bond 2 | $E_r$<br>(eV)<br>Bond 3 | $E_r$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>$C2sp^2$<br>(eV) | $r_{\text{final}}$<br>( $a_0$ ) | $r_{\text{final}}$<br>( $a_0$ ) | $E_{\text{ionized}}$ ( $C2sp^2$ )<br>(eV)<br>Final | $E(C2sp^2)$<br>(eV)<br>Final | $\theta^*$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | $d_1$<br>( $a_0$ ) | $d_2$<br>( $a_0$ ) |
|------------------------------------------------|----------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------------------------|---------------------------------|---------------------------------|----------------------------------------------------|------------------------------|----------------------------|----------------------------|----------------------------|--------------------|--------------------|
| $C-H$ ( $C_1H$ )                               | $C_1$          | -0.54343                | -0.54343                | -0.56690                | 0                       | -153.26945                                | 0.91771                         | 0.82562                         | -16.47951                                          | -16.28864                    | 78.27                      | 101.73                     | 41.39                      | 1.20084            | 0.16785            |
| $C-H$ ( $C_2H$ )                               | $C_2$          | -0.54343                | -0.85035                | -0.56690                | 0                       | -153.57636                                | 0.91771                         | 0.81052                         | -16.78642                                          | -16.59556                    | 76.35                      | 103.65                     | 40.11                      | 1.22423            | 0.19124            |
| $C-H$ ( $C_3H$ )                               | $C_3$          | -0.85035                | -0.85035                | -0.56690                | 0                       | -153.88327                                | 0.91771                         | 0.79597                         | -17.09334                                          | -16.90248                    | 74.42                      | 105.58                     | 38.84                      | 1.24678            | 0.21379            |
| $(H)C_1(H)C_2=N_1C_4$<br>$(H)C_1(H)C_3=N_1C_4$ | $C_1$<br>$C_4$ | -0.85035                | -0.54343                | -0.56690                | 0                       | -153.57636                                | 0.91771                         | 0.81052                         | -16.78642                                          | -16.59556                    | 128.54                     | 51.46                      | 58.65                      | 0.76572            | 0.50501            |
| $(H)C_1(H)C_2=N_1C_4$<br>$(H)C_1(H)C_3=N_1C_4$ | $N_1$<br>$N_4$ | -0.54343                | -0.54343                | 0                       | 0                       |                                           | 0.93084                         | 0.83503                         | -15.91261                                          |                              | 130.61                     | 49.39                      | 60.97                      | 0.71418            | 0.55656            |
| $(H)C_1(H)C_2=N_1C_4$<br>$(H)C_1(H)C_3=N_1C_4$ | $C_1$          | -0.54343                | -0.54343                | -0.56690                | 0                       | -153.26945                                | 0.91771                         | 0.82562                         | -16.47951                                          | -16.28865                    | 129.26                     | 50.74                      | 59.44                      | 0.74824            | 0.52249            |
| $(H)C_1(H)C_2=N_1C_4$<br>$(H)C_1(H)C_3=N_1C_4$ | $N_1$<br>$N_4$ | -0.54343                | -0.54343                | 0                       | 0                       |                                           | 0.93084                         | 0.85503                         | -15.91261                                          |                              | 130.61                     | 49.39                      | 60.97                      | 0.71418            | 0.55656            |
| $N_1(H)C_2=C_1(H)C_4$<br>$N_4(H)C_3=C_1(H)C_4$ | $C_1$          | -0.85035                | -0.85035                | -0.56690                | 0                       | -153.88327                                | 0.91771                         | 0.79597                         | -17.09334                                          | -16.90248                    | 134.24                     | 45.76                      | 58.98                      | 0.75935            | 0.55533            |
| $N_1(H)C_2=C_1(H)C_4$<br>$N_4(H)C_3=C_1(H)C_4$ | $C_1$<br>$C_4$ | -0.85035                | -0.54343                | -0.56690                | 0                       | -153.57636                                | 0.91771                         | 0.81052                         | -16.78642                                          | -16.59556                    | 134.85                     | 45.15                      | 59.72                      | 0.74304            | 0.57165            |

Table 15.300. The energy parameters (eV) of functional groups of pyrimidine.

| Parameters                              | $\overset{\text{N}}{\underset{\text{C}}{\text{C}}}$<br>Group | $\overset{\text{N}}{\underset{\text{C}}{\text{H}}}$<br>Group | $\overset{\text{N}}{\underset{\text{C}}{\text{N}}}$<br>Group |
|-----------------------------------------|--------------------------------------------------------------|--------------------------------------------------------------|--------------------------------------------------------------|
| $f_1$                                   | 0.75                                                         | 1                                                            | 0.75                                                         |
| $n_1$                                   | 2                                                            | 1                                                            | 2                                                            |
| $n_2$                                   | 0                                                            | 0                                                            | 0                                                            |
| $n_3$                                   | 0                                                            | 0                                                            | 0                                                            |
| $C_1$                                   | 0.5                                                          | 0.75                                                         | 0.5                                                          |
| $C_2$                                   | 0.85252                                                      | 1                                                            | 0.91140                                                      |
| $c_1$                                   | 1                                                            | 1                                                            | 1                                                            |
| $c_2$                                   | 0.85252                                                      | 0.91771                                                      | 0.91140                                                      |
| $c_3$                                   | 0                                                            | 1                                                            | 0                                                            |
| $c_4$                                   | 3                                                            | 1                                                            | 3                                                            |
| $c_5$                                   | 0                                                            | 1                                                            | 0                                                            |
| $C_{10}$                                | 0.5                                                          | 0.75                                                         | 0.5                                                          |
| $C_{10}^*$                              | 0.85252                                                      | 1                                                            | 0.91140                                                      |
| $V_e$ (eV)                              | -101.12679                                                   | -37.10024                                                    | -102.01431                                                   |
| $V_p$ (eV)                              | 20.69825                                                     | 13.17125                                                     | 21.41410                                                     |
| $T$ (eV)                                | 34.31559                                                     | 11.58941                                                     | 34.65890                                                     |
| $V_m$ (eV)                              | -17.15779                                                    | -5.79470                                                     | -17.32945                                                    |
| $E_{100}^*$ (eV)                        | 0                                                            | -14.63489                                                    | 0                                                            |
| $\Delta E_{H_{250}}^*$ (eV)             | 0                                                            | -1.13379                                                     | 0                                                            |
| $E_{10}^*$ (eV)                         | 0                                                            | -13.50110                                                    | 0                                                            |
| $E_{10}^*$ (eV)                         | -63.27075                                                    | -31.63539                                                    | -63.27076                                                    |
| $E_{10}^*$ (atom - atom, nosp, AO) (eV) | -2.26759                                                     | -0.56690                                                     | -1.44915                                                     |
| $E_{10}^*$ (eV)                         | -65.53833                                                    | -32.20226                                                    | -64.71988                                                    |
| $\omega$ ( $10^5$ rad/s)                | 49.7272                                                      | 26.4826                                                      | 43.6311                                                      |
| $E_e$ (eV)                              | 32.73133                                                     | 17.43132                                                     | 28.71875                                                     |
| $E_p$ (eV)                              | -0.35806                                                     | -0.26130                                                     | -0.35540                                                     |
| $E_{100}^*$ (eV)                        | 0.19649                                                      | 0.35532                                                      | 0.19649                                                      |
| $E_{100}^*$ (eV)                        | [49]                                                         | Eq. (13.458)                                                 | [49]                                                         |
| $E_{100}^*$ (eV)                        | -0.25982                                                     | -0.08364                                                     | -0.23715                                                     |
| $E_{100}^*$ (eV)                        | 0.14803                                                      | 0.14803                                                      | 0.09457                                                      |
| $E_{100}^*$ (eV)                        | -49.54347                                                    | -32.28590                                                    | -48.82472                                                    |
| $E_{100}^*$ (e, n, n) (eV)              | -14.63489                                                    | -14.63489                                                    | -14.63489                                                    |
| $E_{100}^*$ (e, n, n) (eV)              | 0                                                            | -13.59844                                                    | 0                                                            |
| $E_{100}^*$ (eV)                        | 5.63881                                                      | 3.90454                                                      | 4.92005                                                      |





## PYRAZINE

Pyrazine has the formula  $C_4H_4N_2$  and comprises the pyrimidine molecule with para rather than ortho aromatic nitrogen atoms. The  $C \overset{3e}{=} N$  functional group is equivalent to that of pyrimidine and pyridine given in the corresponding sections. The aromatic  $C \overset{3e}{=} C$  and  $C-H$  functional groups are also equivalent to those of pyrimidine, pyridine, and benzene given in the Aromatic and Heterocyclic Compounds section with the aromaticity maintained by the electrons from nitrogen in the  $C \overset{3e}{=} N$  group which is also aromatic.

The symbols of the functional groups of pyrazine are given in Table 15.303. The corresponding designation of the structure is shown in Figure 71. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of pyrazine are given in Tables 15.304, 15.305, and 15.306, respectively. The total energy of pyrazine given in Table 15.307 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.306 corresponding to functional-group composition of the molecule. The bond angle parameters of pyrazine determined using Eqs. (15.79-15.108) are given in Table 15.308.

Table 15.303. The symbols of functional groups of pyrazine.

| Functional Group      | Group Symbol          |
|-----------------------|-----------------------|
| CC (aromatic bond)    | $C \overset{3e}{=} C$ |
| CH (aromatic)         | $CH$                  |
| $C \overset{3e}{=} N$ | $C \overset{3e}{=} N$ |

Table 15.304. The geometrical bond parameters of pyrazine and experimental values [1].

| Parameter                            | $C \equiv C$<br>Group | $CH$<br>Group       | $C=N$<br>Group      |
|--------------------------------------|-----------------------|---------------------|---------------------|
| $a$ ( $a_0$ )                        | 1.47348               | 1.60061             | 1.47169             |
| $c'$ ( $a_0$ )                       | 1.31468               | 1.03299             | 1.27073             |
| Bond Length $2c'$ ( $\text{\AA}$ )   | 1.39140               | 1.09327             | 1.34489             |
| Exp. Bond Length<br>( $\text{\AA}$ ) | 1.339<br>(pyrazine)   | 1.115<br>(pyrazine) | 1.403<br>(pyrazine) |
| $h_1 c'$ ( $a_0$ )                   | 0.66540               | 1.22265             | 0.74237             |
| $\mu$                                | 0.89223               | 0.64537             | 0.86345             |

Table 15.305. The MO to HO intercept geometrical bond parameters of pyrazine.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{usp}^3, AO)$ .

| Bond                | Atom  | $E_T$<br>(eV)<br>Bond 1 | $E_T$<br>(eV)<br>Bond 2 | $E_T$<br>(eV)<br>Bond 3 | $E_T$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>C2sp <sup>3</sup><br>(eV) | $r_{\text{final}}$<br>( $a_0$ ) | $E_{\text{intercept}}(C2sp^3)$<br>(eV)<br>Final | $E(C2sp^3)$<br>(eV)<br>Final | $\theta'$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | $d_1$<br>( $a_0$ ) | $d_2$<br>( $a_0$ ) |
|---------------------|-------|-------------------------|-------------------------|-------------------------|-------------------------|----------------------------------------------------|---------------------------------|-------------------------------------------------|------------------------------|---------------------------|----------------------------|----------------------------|--------------------|--------------------|
| $C-H$ ( $C_u H$ )   | $C_u$ | -0.54343                | -0.85035                | -0.56690                | 0                       | -153.57636                                         | 0.91771                         | -16.78642                                       | -16.59556                    | 76.35                     | 103.65                     | 40.11                      | 1.22423            | 0.19124            |
| $(H)C_u(H)C_u=NC_u$ | $C_u$ | -0.85035                | -0.54343                | -0.56690                | 0                       | -153.57636                                         | 0.91771                         | -16.78642                                       | -16.59556                    | 128.54                    | 51.46                      | 58.65                      | 0.76572            | 0.50801            |
| $(H)C_u(H)C_u=NC_u$ | N     | -0.54343                | -0.54343                | 0                       | 0                       |                                                    | 0.93084                         | -15.91261                                       |                              | 130.61                    | 49.39                      | 60.97                      | 0.71418            | 0.55656            |
| $N(H)C_u=C_u(H)N$   | $C_u$ | -0.85035                | -0.54343                | -0.56690                | 0                       | -153.57636                                         | 0.91771                         | -16.78642                                       | -16.59556                    | 134.85                    | 45.15                      | 59.72                      | 0.74304            | 0.57165            |

Table 15.306. The energy parameters (eV) of functional groups of pyrazine.

| Parameters                           | C=C<br>Group    | CH<br>Group             | C=N<br>Group    |
|--------------------------------------|-----------------|-------------------------|-----------------|
| $f_1$                                | 0.75            | 1                       | 0.75            |
| $n_1$                                | 2               | 1                       | 2               |
| $n_2$                                | 0               | 0                       | 0               |
| $n_3$                                | 0               | 0                       | 0               |
| $C_1$                                | 0.5             | 0.75                    | 0.5             |
| $C_2$                                | 0.85252         | 1                       | 0.91140         |
| $c_1$                                | 1               | 1                       | 1               |
| $c_2$                                | 0.85252         | 0.91771                 | 0.91140         |
| $c_3$                                | 0               | 1                       | 0               |
| $c_4$                                | 3               | 1                       | 3               |
| $c_5$                                | 0               | 1                       | 0               |
| $C_{10}$                             | 0.5             | 0.75                    | 0.5             |
| $C_{20}$                             | 0.85252         | 1                       | 0.91140         |
| $V_e$ (eV)                           | -101.12679      | -37.10024               | -102.01431      |
| $V_p$ (eV)                           | 20.69825        | 13.17125                | 21.41410        |
| $T$ (eV)                             | 34.31559        | 11.58941                | 34.65890        |
| $V_n$ (eV)                           | -17.15779       | -5.79470                | -17.32945       |
| $E(\pi\pi^*)$ (eV)                   | 0               | -14.63489               | 0               |
| $\Delta E_{H_{2,10}}(\pi\pi^*)$ (eV) | 0               | -1.13379                | 0               |
| $E_T(\pi\pi^*)$ (eV)                 | 0               | -13.50110               | 0               |
| $E_T(\pi\pi^*)$ (eV)                 | -63.27075       | -31.63539               | -63.27076       |
| $E_T(\pi\pi^*)$ (eV)                 | -2.26759        | -0.56690                | -1.44915        |
| $E_T(\pi\pi^*)$ (eV)                 | -65.53833       | -32.20226               | -64.71988       |
| $\omega$ ( $10^5$ rad/s)             | 49.7272         | 26.4826                 | 43.6311         |
| $E_p$ (eV)                           | 32.73133        | 17.43132                | 28.71875        |
| $E_p$ (eV)                           | -0.35806        | -0.26130                | -0.33540        |
| $E_{\text{vib}}$ (eV)                | 0.19649<br>[49] | 0.35532<br>Eq. (13.458) | 0.19649<br>[49] |
| $E_{\text{vib}}$ (eV)                | -0.25982        | -0.08364                | -0.23715        |
| $E_{\text{vib}}$ (eV)                | 0.14803         | 0.14803                 | 0.09457         |
| $E_T(\text{vib})$ (eV)               | -49.54347       | -32.28590               | -48.82472       |
| $E_{\text{vib}}(\pi\pi^*)$ (eV)      | -14.63489       | -14.63489               | -14.63489       |
| $E_{\text{vib}}(\pi\pi^*)$ (eV)      | 0               | -13.59844               | 0               |
| $E_{\text{vib}}(\pi\pi^*)$ (eV)      | 5.63881         | 3.90454                 | 4.92005         |

Table 15.307. The total bond energies of pyrazine calculated using the functional group composition and the energies of Table 15.306 compared to the experimental values [2].

| Formula     | Name     | $\sum C \equiv C$ | $\sum C-H$ | $\sum C=N$ | Calculated Total Bond Energy (eV) | Experimental Total Bond Energy (eV) | Relative Error |
|-------------|----------|-------------------|------------|------------|-----------------------------------|-------------------------------------|----------------|
| $C_4H_4N_2$ | Pyrazine | 2                 | 4          | 4          | 46.57397                          | 46.51380                            | 0.00095        |

Table 15.308. The bond angle parameters of pyrazine and experimental values [1].  $E_T$  is  $E_T(atom - atom, exp, AO)$ .

| Atoms of Angle          | $2c'$ Bond 1 ( $a_0$ ) | $2c'$ Bond 2 ( $a_0$ ) | $2c'$ Terminal Atoms ( $a_0$ ) | $E_{\text{Terminal Atom 1}}$ | Atom 1 Hybridization Designation (Table 15.3B) | $E_{\text{Terminal Atom 2}}$ | Atom 2 Hybridization Designation (Table 15.3B) | $c_2$ Atom 1         | $c_2$ Atom 2         | $C_1$ | $C_2$ | $c_1$ | $c'_1$  | $E_T$ (eV) | $\theta_1$ ( $^\circ$ ) | $\theta_2$ ( $^\circ$ ) | Cal. $\theta$ ( $^\circ$ ) | Exp. $\theta$ ( $^\circ$ )                              |
|-------------------------|------------------------|------------------------|--------------------------------|------------------------------|------------------------------------------------|------------------------------|------------------------------------------------|----------------------|----------------------|-------|-------|-------|---------|------------|-------------------------|-------------------------|----------------------------|---------------------------------------------------------|
| $\angle CCC$ (aromatic) | 2.62936                | 2.62936                | 4.5585                         | -17.17218                    | 20                                             | -17.17218                    | 20                                             | 0.79232              | 0.79232              | 1     | 1     | 1     | 0.79232 | -1.85836   |                         |                         | 120.19                     | 120 [50-52] (benzene) 118.3 (pyridine) 118.5 (pyridine) |
| $\angle CCH$ (aromatic) |                        |                        |                                |                              |                                                |                              |                                                |                      |                      |       |       |       |         |            |                         |                         |                            | 120 [50-52] (benzene) 121.3 (pyridine)                  |
| $\angle HCN$            | 2.06598                | 2.54147                | 3.9497                         | -14.82575                    | 1                                              | -14.53414                    | N                                              | 0.91771              | 0.91140 Eq. (15.116) | 0.75  | 1     | 0.75  | 0.99312 | 0          |                         |                         | 117.65                     | 115.9 (pyridine)                                        |
| $\angle CCH$            |                        |                        |                                |                              |                                                |                              |                                                |                      |                      |       |       |       |         |            |                         |                         |                            | 123.9 (pyridine)                                        |
| $\angle NCC$            | 2.54147                | 2.62936                | 4.4045                         | -14.53414                    | N                                              | -17.09334                    | 7                                              | 0.91140 Eq. (15.116) | 0.79597              | 1     | 1     | 1     | 0.85368 | -1.44915   |                         |                         | 125.54                     | 115.6 (pyrazine)                                        |
| $\angle C'NC$           | 2.54147                | 2.54147                | 4.3359                         | -17.71560                    | 24                                             | -17.71560                    | 24                                             | 0.76801              | 0.76801              | 1     | 1     | 1     | 0.76801 | -1.85836   |                         |                         | 117.09                     | 116.8 (pyrimidine)                                      |

## QUINOLINE

Quinoline has the formula  $C_9H_7N$  and comprises the naphthalene molecule with one  $CH$  group replaced by a nitrogen atom which gives rise to a  $C=N^{3e}$  functional group. The aromatic  $C=C^{3e}$  and  $C-H$  functional groups are equivalent to those of naphthalene given in the corresponding section with the aromaticity maintained by the electrons from nitrogen in the  $C=N^{3e}$  group which is also aromatic. The  $C-C$  functional group is also equivalent to that of naphthalene. The bonding in quinoline can be further considered as a linear combination of the naphthalene and pyridine groups wherein the  $C=N^{3e}$  group is equivalent to that of pyridine, pyrimidine, and pyrazine as given in the corresponding sections.

The symbols of the functional groups of quinoline are given in Table 15.309. The corresponding designation of the structure is shown in Figure 72. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of quinoline are given in Tables 15.310, 15.311, and 15.312, respectively. The total energy of quinoline given in Table 15.313 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.312 corresponding to functional-group composition of the molecule. The bond angle parameters of quinoline determined using Eqs. (15.79-15.108) are given in Table 15.314.

Table 15.309. The symbols of functional groups of quinoline.

| Functional Group            | Group Symbol |
|-----------------------------|--------------|
| $CC$ (aromatic bond)        | $C=C^{3e}$   |
| $CH$ (aromatic)             | $CH$         |
| $C_b - C_b$ (bridging bond) | $C - C$      |
| $C_{a,d}^{3e} = N$          | $C=N^{3e}$   |

Table 15.31.0. The geometrical bond parameters of quinoline and experimental values [1].

| Parameter                            | $C=C$<br>Group               | $CH$<br>Group      | $C-C$<br>Group        | $C=N$<br>Group      |
|--------------------------------------|------------------------------|--------------------|-----------------------|---------------------|
| $a$ ( $a_0$ )                        | 1.47348                      | 1.60061            | 1.75607               | 1.47169             |
| $c'$ ( $a_0$ )                       | 1.31468                      | 1.03299            | 1.32517               | 1.27073             |
| Bond Length $2c'$ ( $\text{\AA}$ )   | 1.39140                      | 1.09327            | 1.40250               | 1.34489             |
| Exp. Bond Length<br>( $\text{\AA}$ ) | 1.40 (avg.)<br>(naphthalene) | 1.101<br>(benzene) | 1.42<br>(naphthalene) | 1.340<br>(pyridine) |
| $b,c$ ( $a_0$ )                      | 0.66540                      | 1.22265            | 1.15226               | 0.74237             |
| $e$                                  | 0.89223                      | 0.64537            | 0.75462               | 0.86345             |

Table 15.31.1. The MO to HO intercept geometrical bond parameters of quinoline.  $E_T$  is  $E_T(atom - atom, msp^3 AO)$ .

| Bond                 | Atom  | $E_T$<br>(eV)<br>Bond 1 | $E_T$<br>(eV)<br>Bond 2 | $E_T$<br>(eV)<br>Bond 3 | $E_T$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>$C2_{sp^3}$<br>(eV) | $r_{final}$<br>( $a_0$ ) | $E_{C_{2sp^3}}$<br>(eV)<br>Final | $E(C2_{sp^3})$<br>(eV)<br>Final | $\theta'$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | $d_1$<br>( $a_0$ ) | $d_2$<br>( $a_0$ ) |
|----------------------|-------|-------------------------|-------------------------|-------------------------|-------------------------|----------------------------------------------|--------------------------|----------------------------------|---------------------------------|---------------------------|----------------------------|----------------------------|--------------------|--------------------|
| $C-H$ ( $C_uH$ )     | $C_u$ | -0.85035                | -0.54343                | -0.56690                | 0                       | -153.57656                                   | 0.91771                  | -16.78642                        | -16.59556                       | 76.35                     | 103.65                     | 40.11                      | 1.23423            | 0.19124            |
| $C-H$ ( $C_uH$ )     | $C_u$ | -0.85035                | -0.85035                | -0.56690                | 0                       | -153.88327                                   | 0.91771                  | -17.09334                        | -16.90248                       | 74.42                     | 105.58                     | 38.84                      | 1.24678            | 0.21379            |
| $N(H)C_u=C_u(H)$     | $C_u$ | -0.85035                | -0.54343                | -0.56690                | 0                       | -153.57656                                   | 0.91771                  | -16.78642                        | -16.59556                       | 134.85                    | 45.15                      | 59.72                      | 0.74304            | 0.57165            |
| $(H)C_u=C_u(H)$      | $C_u$ | -0.85035                | -0.85035                | -0.56690                | 0                       | -153.88327                                   | 0.91771                  | -17.09334                        | -16.90248                       | 134.24                    | 45.76                      | 58.98                      | 0.75935            | 0.55533            |
| $(H)C_u(C_u)C_u=C_u$ | $C_u$ | -0.85035                | -0.85035                | -0.28345                | 0                       | -153.59983                                   | 0.91771                  | -16.80989                        | -16.61903                       | 134.81                    | 45.19                      | 59.66                      | 0.74430            | 0.57038            |
| $N(C_u)C_u=C_u$      | $C_u$ | -0.85035                | -0.54343                | -0.28345                | 0                       | -153.29292                                   | 0.91771                  | -16.50298                        | -16.31211                       | 135.42                    | 44.58                      | 60.42                      | 0.72743            | 0.58725            |
| $C_u(H)C_u=N$        | $C_u$ | -0.85035                | -0.54343                | -0.56690                | 0                       | -153.57656                                   | 0.91771                  | -16.78642                        | -16.59556                       | 128.54                    | 51.46                      | 58.65                      | 0.76572            | 0.50801            |
| $C_u(H)C_u=N$        | $N$   | -0.54343                | -0.54343                | 0                       | 0                       |                                              | 0.93084                  | -15.91561                        |                                 | 130.61                    | 49.39                      | 60.97                      | 0.71418            | 0.55656            |
| $C_u(C_u)C_u=N$      | $C_u$ | -0.85035                | -0.54343                | -0.28345                | 0                       | -153.29291                                   | 0.91771                  | -16.50297                        | -16.31211                       | 128.21                    | 50.79                      | 59.38                      | 0.74960            | 0.52113            |
| $(H)C_u=C_u(C_u)C_u$ | $C_u$ | -0.85035                | -0.85035                | -0.28345                | 0                       | -153.59983                                   | 0.91771                  | -16.80989                        | -16.61903                       | 95.01                     | 84.99                      | 44.41                      | 1.25451            | 0.07066            |
| $N(C_u)C_u=C_u$      | $C_u$ | -0.85035                | -0.54343                | -0.28345                | 0                       | -153.29292                                   | 0.91771                  | -16.50298                        | -16.31211                       | 96.31                     | 83.69                      | 45.33                      | 1.23456            | 0.09061            |

Table 15.312. The energy parameters (eV) of functional groups of quinoline.

| Parameters                    | C=C<br>Group | CH<br>Group                | C-C<br>Group | C=N<br>Group |
|-------------------------------|--------------|----------------------------|--------------|--------------|
| $f_1$                         | 0.75         | 1                          | 1            | 0.75         |
| $n_1$                         | 2            | 1                          | 1            | 2            |
| $n_2$                         | 0            | 0                          | 0            | 0            |
| $n_3$                         | 0            | 0                          | 0            | 0            |
| $C_1$                         | 0.5          | 0.75                       | 0.5          | 0.5          |
| $C_2$                         | 0.85252      | 1                          | 1            | 0.91140      |
| $C_3$                         | 1            | 1                          | 1            | 1            |
| $C_4$                         | 0.85252      | 0.91771                    | 0.85252      | 0.91140      |
| $C_5$                         | 0            | 1                          | 0            | 0            |
| $C_6$                         | 3            | 1                          | 2            | 3            |
| $C_7$                         | 0            | 1                          | 0            | 0            |
| $C_{10}$                      | 0.5          | 0.75                       | 0.5          | 0.5          |
| $C_{10}$                      | 0.85252      | 1                          | 1            | 0.91140      |
| $V_c$ (eV)                    | -101.12679   | -37.10024                  | -34.43791    | -102.01431   |
| $V_c$ (eV)                    | 20.69825     | 13.17125                   | 10.26723     | 21.41410     |
| $T$ (eV)                      | 34.31559     | 11.58941                   | 9.80539      | 34.65890     |
| $V_m$ (eV)                    | -17.15779    | -5.79470                   | -4.90270     | -17.32945    |
| $E_{\text{HOMO}}$ (eV)        | 0            | -14.63489                  | -14.63489    | 0            |
| $\Delta E_{\text{HOMO}}$ (eV) | 0            | -1.13379                   | -1.13379     | 0            |
| $E_{\text{HOMO}}$ (eV)        | 0            | -13.50110                  | -13.50110    | 0            |
| $E_{\text{HOMO}}$ (eV)        | -63.27075    | -31.63539                  | -31.63529    | -63.27076    |
| $E_{\text{HOMO}}$ (eV)        | -2.26759     | -0.56690                   | -0.56690     | -1.44915     |
| $E_{\text{HOMO}}$ (eV)        | -65.53833    | -32.20226                  | -32.20226    | -64.71988    |
| $\omega$ ( $10^5$ rad/s)      | 49.7272      | 26.4826                    | 23.6343      | 43.6311      |
| $E_{\text{HOMO}}$ (eV)        | 32.73133     | 17.43132                   | 15.55648     | 28.71875     |
| $E_{\text{HOMO}}$ (eV)        | -0.35806     | -0.26130                   | -0.25127     | -0.33540     |
| $E_{\text{HOMO}}$ (eV)        | 0.19649      | 0.35532                    | 0.12312      | 0.19649      |
| $E_{\text{HOMO}}$ (eV)        | [49]         | $E_{\text{HOMO}}$ (13.458) | [2]          | [49]         |
| $E_{\text{HOMO}}$ (eV)        | -0.25982     | -0.08364                   | -0.18971     | -0.23715     |
| $E_{\text{HOMO}}$ (eV)        | 0.14803      | 0.14803                    | 0.14803      | 0.09457      |
| $E_{\text{HOMO}}$ (eV)        | 49.54347     | -32.28590                  | -32.39198    | -48.82472    |
| $E_{\text{HOMO}}$ (eV)        | -14.63489    | -14.63489                  | -14.63489    | -14.63489    |
| $E_{\text{HOMO}}$ (eV)        | 0            | -13.59844                  | 0            | 0            |
| $E_{\text{HOMO}}$ (eV)        | 5.63881      | 3.90454                    | 3.12220      | 4.92005      |

Table 15.313. The total bond energies of quinoline calculated using the functional group composition and the energies of Table 15.312 compared to the experimental values [2]. 1.

| Formula                        | Name      | $\text{C}=\text{C}$ | $\text{C}-\text{C}$ | $\text{C}-\text{H}$ | $\text{C}-\text{N}$ | Calculated<br>Total Bond Energy<br>(eV) | Experimental<br>Total Bond Energy<br>(eV) | Relative Error |
|--------------------------------|-----------|---------------------|---------------------|---------------------|---------------------|-----------------------------------------|-------------------------------------------|----------------|
| $\text{C}_8\text{H}_7\text{N}$ | Quinoline | 8                   | 7                   | 7                   | 2                   | 85.40433                                | 85.48607                                  | 0.0078         |

Table 15.314. The bond angle parameters of quinoline and experimental values [1].  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{map}, \text{AO})$ .

| Atoms of Angle                 | $2c'_1$<br>Bond 1<br>( $\sigma_a$ ) | $2c'_2$<br>Bond 2<br>( $\sigma_a$ ) | $2c'$<br>Terminal<br>Atoms<br>( $\sigma_a$ ) | $E_{\text{calc/absc}}$<br>Atom 1 | Atom 1<br>Hybridization<br>Designation<br>(Table 15.3B) | $E_{\text{calc/absc}}$<br>Atom 2 | Atom 2<br>Hybridization<br>Designation<br>(Table 15.3B) | $c_2$<br>Atom 1 | $c_2$<br>Atom 2 | $C_1$ | $C_2$ | $C_1$ | $C_2$ | $\zeta_1$ | $\zeta_2$ | $E_T$<br>(eV) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | Cal. $\theta$<br>( $^\circ$ ) | Exp. $\theta$<br>( $^\circ$ ) |
|--------------------------------|-------------------------------------|-------------------------------------|----------------------------------------------|----------------------------------|---------------------------------------------------------|----------------------------------|---------------------------------------------------------|-----------------|-----------------|-------|-------|-------|-------|-----------|-----------|---------------|----------------------------|----------------------------|-------------------------------|-------------------------------|
| $\angle \text{CCC}$            | 2.62936                             | 2.65034                             | 4.5585                                       | -17.17218                        | 20                                                      | -17.17218                        | 20                                                      | 0.79232         | 0.79232         | 1     | 1     | 1     | 1     | 0.79232   |           | -1.85836      |                            |                            | 119.40                        | 119.4<br>(naphthalene)        |
| $\angle \text{CCH}$            |                                     |                                     |                                              |                                  |                                                         |                                  |                                                         |                 |                 |       |       |       |       |           |           |               | 119.40                     |                            | 120.30                        |                               |
| $\angle \text{C}_i\text{NC}_o$ | 2.54147                             | 2.54147                             | 4.3818                                       | -17.43216                        | 22                                                      | -17.71560                        | 24                                                      | 0.78050         | 0.76801         | 1     | 1     | 1     | 1     | 0.77426   |           | -1.85836      |                            |                            | 119.10                        |                               |



## ISOQUINOLINE

Isoquinoline has the formula  $C_9H_7N$  and comprises the naphthalene molecule with one  $CH$  group replaced by a nitrogen atom which gives rise to a  $C \overset{3e}{=} N$  functional group. Isoquinoline is also equivalent to quinoline with the nitrogen in the meta rather than the ortho position relative to the benzene ring of the molecule. The aromatic  $C \overset{3e}{=} C$  and  $C-H$  functional groups are equivalent to those of naphthalene given in the corresponding section with the aromaticity maintained by the electrons from nitrogen in the  $C \overset{3e}{=} N$  group which is also aromatic. The  $C-C$  functional group is also equivalent to that of naphthalene. The bonding in isoquinoline can be further considered as a linear combination of the naphthalene and pyridine groups wherein the  $C \overset{3e}{=} N$  group is equivalent to that of pyridine, pyrimidine, pyrazine, and quinoline as given in the corresponding sections.

The symbols of the functional groups of isoquinoline are given in Table 15.315. The corresponding designation of the structure is shown in Figure 73. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of isoquinoline are given in Tables 15.316, 15.317, and 15.318, respectively. The total energy of isoquinoline given in Table 15.319 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.318 corresponding to functional-group composition of the molecule. The bond angle parameters of isoquinoline determined using Eqs. (15.79-15.108) are given in Table 15.320.

Table 15.315. The symbols of functional groups of isoquinoline.

| Functional Group            | Group Symbol          |
|-----------------------------|-----------------------|
| $CC$ (aromatic bond)        | $C \overset{3e}{=} C$ |
| $CH$ (aromatic)             | $CH$                  |
| $C_b - C_b$ (bridging bond) | $C - C$               |
| $C_{a,d} \overset{3e}{=} N$ | $C \overset{3e}{=} N$ |

Table 15.316. The geometrical bond parameters of isoquinoline and experimental values [1].

| Parameter                          | C=C Group                 | CH Group        | C-C Group          | C=N Group        |
|------------------------------------|---------------------------|-----------------|--------------------|------------------|
| $a$ ( $a_0$ )                      | 1.47348                   | 1.60061         | 1.75607            | 1.47169          |
| $c'$ ( $a_0$ )                     | 1.31468                   | 1.03299         | 1.32517            | 1.27073          |
| Bond Length $2c'$ ( $\text{\AA}$ ) | 1.39140                   | 1.09327         | 1.40250            | 1.34489          |
| Exp. Bond Length ( $\text{\AA}$ )  | 1.40 (avg.) (naphthalene) | 1.101 (benzene) | 1.42 (naphthalene) | 1.340 (pyridine) |
| $h, c$ ( $a_0$ )                   | 0.66540                   | 1.22265         | 1.15226            | 0.74237          |
| $c$                                | 0.89223                   | 0.64537         | 0.75462            | 0.86345          |

Table 15.317. The MO to HO intercept geometrical bond parameters of isoquinoline.  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{resp. } \text{AO})$ .

| Bond                            | Atom  | $E_r$ (eV) Bond 1 | $E_r$ (eV) Bond 2 | $E_r$ (eV) Bond 3 | $E_r$ (eV) Bond 4 | Final Total Energy $C_{2sp^3}$ (eV) | $r_{\text{final}}$ ( $a_0$ ) | $E_{\text{total}}(C_{2sp^3})$ (eV) Final | $\theta'$ ( $^\circ$ ) | $\theta_1$ ( $^\circ$ ) | $\theta_2$ ( $^\circ$ ) | $d_1$ ( $a_0$ ) | $d_2$ ( $a_0$ ) |
|---------------------------------|-------|-------------------|-------------------|-------------------|-------------------|-------------------------------------|------------------------------|------------------------------------------|------------------------|-------------------------|-------------------------|-----------------|-----------------|
| C-H ( $C_a$ H)                  | $C_a$ | -0.85035          | -0.54343          | -0.56690          | 0                 | -153.57636                          | 0.91771                      | -16.78642                                | 76.35                  | 103.65                  | 40.11                   | 1.22423         | 0.19124         |
| C-H ( $C_b$ H)                  | $C_b$ | -0.85035          | -0.54343          | -0.56690          | 0                 | -153.57636                          | 0.91771                      | -16.78642                                | 76.35                  | 103.65                  | 40.11                   | 1.22423         | 0.19124         |
| C-H ( $C_c$ H)                  | $C_c$ | -0.85035          | -0.85035          | -0.56690          | 0                 | -153.88327                          | 0.91771                      | -17.09334                                | 74.42                  | 105.58                  | 38.84                   | 1.24678         | 0.21379         |
| $N(H)C_a=C_d$                   | $C_a$ | -0.85035          | -0.54343          | -0.56690          | 0                 | -153.57636                          | 0.91771                      | -16.78642                                | 134.85                 | 45.15                   | 59.72                   | 0.74394         | 0.57165         |
| $N(H)C_b=C_c$                   | $C_b$ | -0.85035          | -0.54343          | -0.56690          | 0                 | -153.57636                          | 0.91771                      | -16.78642                                | 134.85                 | 45.15                   | 59.72                   | 0.74394         | 0.57165         |
| $(H)C_c=C_d$                    | $C_c$ | -0.85035          | -0.85035          | -0.56690          | 0                 | -153.88327                          | 0.91771                      | -17.09334                                | 134.24                 | 45.76                   | 58.98                   | 0.75935         | 0.55533         |
| $(H)C_c(C_c)C_d=C_{\text{res}}$ | $C_d$ | -0.85035          | -0.85035          | -0.28345          | 0                 | -153.59983                          | 0.91771                      | -16.80989                                | 134.81                 | 45.19                   | 59.66                   | 0.74430         | 0.57038         |
| $C_a(H)C_d=N$                   | $C_a$ | -0.85035          | -0.54343          | -0.56690          | 0                 | -153.57636                          | 0.91771                      | -16.78642                                | 128.54                 | 51.46                   | 58.65                   | 0.76572         | 0.50501         |
| $C_c(H)C_b=N$                   | $C_b$ | -0.85035          | -0.54343          | -0.56690          | 0                 | -153.57636                          | 0.91771                      | -16.78642                                | 128.54                 | 51.46                   | 58.65                   | 0.76572         | 0.50501         |
| $C_a(H)C_d=N$                   | $N$   | -0.54343          | -0.54343          | 0                 | 0                 |                                     | 0.93084                      | -15.91261                                | 130.61                 | 49.39                   | 60.97                   | 0.71418         | 0.55656         |
| $C_c(H)C_b=N$                   | $C_d$ | -0.85035          | -0.85035          | -0.28345          | 0                 | -153.59983                          | 0.91771                      | -16.80989                                | 95.01                  | 84.99                   | 44.41                   | 1.25451         | 0.07066         |

Table 15.318. The energy parameters (eV) of functional groups of isosquinoine.

| Parameters                                                   | $C^{\infty}$<br>Group | $C^H$<br>Group | $C-C$<br>Group | $C-N$<br>Group |
|--------------------------------------------------------------|-----------------------|----------------|----------------|----------------|
| $f_i$                                                        | 0.75                  | 1              | 1              | 0.75           |
| $n_1$                                                        | 2                     | 1              | 1              | 2              |
| $n_2$                                                        | 0                     | 0              | 0              | 0              |
| $n_3$                                                        | 0                     | 0              | 0              | 0              |
| $C_1$                                                        | 0.5                   | 0.75           | 0.5            | 0.5            |
| $C_2$                                                        | 0.85252               | 1              | 1              | 0.91140        |
| $C_3$                                                        | 1                     | 1              | 1              | 1              |
| $C_4$                                                        | 0.85252               | 0.91771        | 0.85252        | 0.91140        |
| $C_5$                                                        | 0                     | 1              | 0              | 0              |
| $C_6$                                                        | 3                     | 1              | 2              | 3              |
| $C_7$                                                        | 0                     | 1              | 0              | 0              |
| $C_{10}$                                                     | 0.5                   | 0.75           | 0.5            | 0.5            |
| $C_{20}$                                                     | 0.85252               | 1              | 1              | 0.91140        |
| $V_e$ (eV)                                                   | -101.12679            | -37.10024      | -34.43791      | -102.01431     |
| $V_s$ (eV)                                                   | 20.69825              | 13.17125       | 10.26723       | 21.41410       |
| $T$ (eV)                                                     | 34.31559              | 11.58941       | 9.80539        | 34.65890       |
| $V_m$ (eV)                                                   | -17.15779             | -5.79470       | -4.90270       | -17.32945      |
| $E_{(10\text{ m})}$ (eV)                                     | 0                     | -14.63489      | -14.63489      | 0              |
| $\Delta E_{(10\text{ m})}$ (eV)                              | 0                     | -1.13379       | -1.13379       | 0              |
| $E_{(10\text{ m})}$ (eV)                                     | 0                     | -13.50110      | -13.50110      | 0              |
| $E_{(10\text{ m})}$ (eV)                                     | -63.27075             | -31.63539      | -31.63529      | -63.27076      |
| $E_{(atom - atom, nsp^1, O)}$ (eV)                           | -2.26759              | -0.56690       | -0.56690       | -1.44915       |
| $E_{(10\text{ m})}$ (eV)                                     | -65.53833             | -32.20226      | -32.20226      | -64.71988      |
| $\omega$ ( $10^5 \text{ rad/s}$ )                            | 49.7272               | 26.4826        | 23.6343        | 43.6311        |
| $E_c$ (eV)                                                   | 32.73133              | 17.43132       | 15.55648       | 28.71875       |
| $E_b$ (eV)                                                   | -0.35806              | -0.26130       | -0.25127       | -0.33540       |
| $E_{\text{kin}}$ (eV)                                        | 0.19649               | 0.35532        | 0.12312        | 0.19649        |
|                                                              | [49]                  | Eg. (13.458)   | [2]            | [49]           |
| $E_{\text{oe}}$ (eV)                                         | -0.25982              | -0.08364       | -0.18971       | -0.23715       |
| $E_{\text{ox}}$ (eV)                                         | 0.14803               | 0.14803        | 0.14803        | 0.09457        |
| $E_{(10\text{ m})}$ (eV)                                     | -49.54347             | -32.28590      | -32.39198      | -48.82472      |
| $E_{\text{min}}$ ( $\epsilon_{\text{e}}, 10\text{ m}$ ) (eV) | -14.63489             | -14.63489      | -14.63489      | -14.63489      |
| $E_{\text{min}}$ ( $\epsilon_{\text{e}}, 10\text{ m}$ ) (eV) | 0                     | -13.59844      | 0              | 0              |
| $E_{(10\text{ m})}$ (eV)                                     | 5.63881               | 3.90454        | 3.12220        | 4.92005        |

Table 15.319. The total bond energies of isoquinoline calculated using the functional group composition and the energies of Table 15.318 compared to the experimental values [2].

| Formula                        | Name         | $\text{C}=\text{C}$ | $\text{C}-\text{H}$ | $\text{C}-\text{C}$ | $\text{C}=\text{N}$ | Group | Calculated<br>Total Bond Energy<br>(eV) | Experimental<br>Total Bond Energy<br>(eV) | Relative Error |
|--------------------------------|--------------|---------------------|---------------------|---------------------|---------------------|-------|-----------------------------------------|-------------------------------------------|----------------|
| $\text{C}_9\text{H}_7\text{N}$ | Isoquinoline | 8                   | 7                   | 1                   | 2                   |       | 85.40453                                | 85.44338                                  | 0.00046        |

Table 15.320. The bond angle parameters of isoquinoline and experimental values [1].  $E_r$  is  $E_r(\text{atom} - \text{atom}, \text{msp}, \text{AO})$ .

| Table 15.320. The bond angle parameters of isocytidine and experimental values [1]. $E_r$ is $E_r(\text{atom} - \text{atom}, \text{msp}^2, \text{AO})$ . |                              |                              |                                        |                                    |                                                          |                                    |                                                          |                 |                 |       |       |       |         |               |                            |                            |                            |                               |                               |  |  |  |  |  |  |
|----------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------|------------------------------|----------------------------------------|------------------------------------|----------------------------------------------------------|------------------------------------|----------------------------------------------------------|-----------------|-----------------|-------|-------|-------|---------|---------------|----------------------------|----------------------------|----------------------------|-------------------------------|-------------------------------|--|--|--|--|--|--|
| Atoms of Angle                                                                                                                                           | $2c'$<br>Bond 1<br>( $a_n$ ) | $2c'$<br>Bond 2<br>( $a_n$ ) | $2c'$<br>Terminal<br>Atom<br>( $a_n$ ) | $E_r^{\text{calc}}(\text{Atom 1})$ | Atom 1<br>Hybridization<br>Designation<br>(Table 15.318) | $E_r^{\text{calc}}(\text{Atom 2})$ | Atom 2<br>Hybridization<br>Designation<br>(Table 15.318) | $c_2$<br>Atom 1 | $c_2$<br>Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c'_1$  | $E_r$<br>(eV) | $\theta_r$<br>( $^\circ$ ) | $\theta_l$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | Cat. $\theta$<br>( $^\circ$ ) | Exp. $\theta$<br>( $^\circ$ ) |  |  |  |  |  |  |
| $\angle C'CC$                                                                                                                                            | 2.62936                      | 2.65034                      | 4.5585                                 | -17.17218                          | 20<br>(Table 15.318)                                     | -17.17218                          | 20<br>(Table 15.318)                                     | 0.79232         | 0.79232         | 1     | 1     | 1     | 0.79232 | -1.85836      |                            |                            |                            | 119.40                        | 119.4                         |  |  |  |  |  |  |
| $\angle C'CH$                                                                                                                                            | 2.54147                      | 2.54147                      | 4.3818                                 | -17.63216                          | 22                                                       |                                    |                                                          |                 |                 |       |       |       |         |               |                            | 119.40                     |                            | 120.30                        | (naphthalene)                 |  |  |  |  |  |  |
| $\angle C'NC'_k$                                                                                                                                         | 2.54147                      | 2.54147                      | 4.3818                                 | -17.63216                          | 24                                                       |                                    |                                                          | 0.78050         | 0.78001         | 1     | 1     | 1     | 0.77436 | -1.85836      |                            |                            |                            | 119.10                        |                               |  |  |  |  |  |  |

## INDOLE

Indole having the formula  $C_8H_7N$  comprises a phenyl moiety with a conjugated five-membered ring which comprises pyrrole except that one of the double bonds is part of the aromatic ring. The structure is shown in Figure. 74. The aromatic  $C=C$  and  $C-H$  functional groups of the phenyl moiety are equivalent to those of benzene given in the Aromatic and Heterocyclic Compounds section. The  $CH$ ,  $NH$ , and  $C_d = C_e$  groups of the pyrrole-type ring are equivalent to the corresponding groups of pyrrole, furan, and thiophene where present as given in the corresponding sections. The  $C_b - C_d$  single bond of aryl carbon to the  $C_d = C_e$  bond is also a functional group. This group is equivalent to the  $C-C(O)$  group of benzoic acids with regard to  $\Delta E_{H_1MO}(AO/HO)$  in Eq. (15.42) and  $E_T(atom - atom, msp^3.AO)$  in Eq. (15.52) both being  $-1.29147 \text{ eV}$ . This energy is a linear combination of  $\frac{-1.13379 \text{ eV}}{2}$ ,  $E_T(atom - atom, msp^3.AO)$  of the  $C-H$  group that the  $C_b - C_d$  and  $C-C(O)$  groups replace, and that of an independent  $C2sp^3 HO$ ,  $-0.72457 \text{ eV}$  (Eq. (14.151)). However, as in the case of pyrrole, the indole hybridization term  $c_2$  is the aromatic  $c_2(benzeneC2sp^3HO) = 0.85252$  to match the aryl  $C2sp^3 HO$ , and the energy terms corresponding to oscillation in the transition state correspond to indole.

As in the case of pyrrole, the  $C-N-C$ -bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with  $n_1 = 2$  in Eqs. (15.42) and (15.52). The hybridization factor  $c_2(arylC2sp^3HO \text{ to } N) = 0.84665$  (Eq. (15.152)) matches the aromatic character of the  $C2sp^3 HO$ s to the  $N$  atom of the  $NH$  group, and  $C_2$  and  $C_{2o}$  in Eqs. (15.42) and (15.52) become that of benzene given by Eq. (15.143),  $C_2(benzeneC2sp^3HO) = 0.85252$ . Furthermore,  $\Delta E_{H_1MO}(AO/HO)$  in Eq. (15.42) and  $E_T(atom - atom, msp^3.AO)$  in Eq. (15.52) are both  $-2.42526 \text{ eV}$  which is a linear combination of  $\frac{-1.13379 \text{ eV}}{2}$ ,  $E_T(atom - atom, msp^3.AO)$  of the  $C-H$  group that the  $C_e - N$  bond replaces, and  $-1.85836 \text{ eV}$  (Eq. (14.513)) which is equivalent to the corresponding component of the  $C-N-C$ -bond of pyrrole.

The symbols of the functional groups of indole are given in Table 15.321. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of indole are given in Tables 15.322, 15.323, and 15.324, respectively. The total energy of indole given in Table 15.325 was calculated as the  
 5 sum over the integer multiple of each  $E_p(\text{Group})$  of Table 15.324 corresponding to functional-group composition of the molecule. The bond angle parameters of indole determined using Eqs. (15.79-15.108) are given in Table 15.326.

Table 15.321. The symbols of functional groups of indole.

| Functional Group        | Group Symbol          |
|-------------------------|-----------------------|
| CC (aromatic bond)      | $\overset{3e}{C} = C$ |
| CH (aromatic)           | CH (i)                |
| $C_d = C_e$ double bond | $C = C$               |
| $C_b - C_d$             | $C - C$               |
| CH                      | CH (ii)               |
| $C_e - N - C_e$         | $C - N - C$           |
| NH group                | NH                    |

Table 15.322. The geometrical bond parameters of indole and experimental values [1].

| Parameter                          | C=C Group       | C-H (i) Group   | C=C Group       | C-H (ii) Group  | C-C Group       | C-N-C Group     | NH Group        |
|------------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $a$ ( $a_0$ )                      | 1.47348         | 1.60661         | 1.45103         | 1.53380         | 1.81395         | 1.44394         | 1.24428         |
| $c'$ ( $a_0$ )                     | 1.31468         | 1.03299         | 1.30463         | 1.01120         | 1.34683         | 1.30144         | 0.94134         |
| Bond Length $2c'$ ( $\text{\AA}$ ) | 1.39140         | 1.09327         | 1.38076         | 1.07021         | 1.42542         | 1.37738         | 0.996270        |
| Exp. Bond Length ( $\text{\AA}$ )  | 1.399 (benzene) | 1.101 (benzene) | 1.382 (pyrrole) | 1.076 (pyrrole) | 1.417 (pyrrole) | 1.370 (pyrrole) | 0.996 (pyrrole) |
| $h_a c'$ ( $a_0$ )                 | 0.66540         | 1.22265         | 0.63517         | 1.15326         | 1.21510         | 0.62548         | 0.81370         |
| $e$                                | 0.89223         | 0.64537         | 0.89910         | 0.65928         | 0.74248         | 0.90131         | 0.75653         |

Table 15.323. The MO to HO intercept geometrical bond parameters of indole.  $R_i$  is an alkyl group and  $R', R''$  are H or alkyl groups.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{msp}, \text{AO})$ .

| Bond                    | Atom  | $E_T$ (eV) Bond 1 | $E_T$ (eV) Bond 2 | $E_T$ (eV) Bond 3 | $E_T$ (eV) Bond 4 | Final Total Energy $C^{2sp^3}$ (eV) | $r_{\text{final}}$ ( $a_0$ ) | $E_{\text{total}}(C^{2sp^3})$ Final | $E(C^{2sp^3})$ Final | $\theta'$ ( $^\circ$ ) | $\theta_i$ ( $^\circ$ ) | $\theta_z$ ( $^\circ$ ) | $d_i$ ( $a_0$ ) | $d_z$ ( $a_0$ ) |
|-------------------------|-------|-------------------|-------------------|-------------------|-------------------|-------------------------------------|------------------------------|-------------------------------------|----------------------|------------------------|-------------------------|-------------------------|-----------------|-----------------|
| $C-H(C, H)$             | $C_u$ | -0.85035          | -0.85035          | -0.56690          | 0                 | -153.88327                          | 0.91771                      | -17.09334                           | -16.90248            | 74.42                  | 105.58                  | 38.84                   | 1.24678         | 0.21379         |
| $C_u = HC_u = C_{u,ke}$ | $C_u$ | -0.85035          | -0.85035          | -0.56690          | 0                 | -153.88327                          | 0.91771                      | -17.09334                           | -16.90248            | 134.24                 | 45.76                   | 58.98                   | 0.75935         | 0.55533         |
| $C_u = (C_u)C_u = C_i$  | $C_u$ | -0.85035          | -0.64574          | -0.85035          | 0                 | -153.96212                          | 0.91771                      | -17.17218                           | -16.98132            | 134.09                 | 45.91                   | 58.79                   | 0.76344         | 0.55124         |
| $C_u = C_i(N)C_u$       | $C_u$ | -0.60631          | -0.85035          | -0.85035          | 0                 | -153.92270                          | 0.91771                      | -17.13276                           | -16.94190            | 134.16                 | 45.84                   | 58.89                   | 0.76140         | 0.55328         |
| $C_u = C_i(N)C_u$       | $C_u$ | -0.85035          | -0.85035          | -0.64574          | 0                 | -153.96212                          | 0.91771                      | -17.17218                           | -16.98132            | 87.89                  | 92.11                   | 40.66                   | 1.37597         | 0.02914         |
| $C_u(H)C_u - C_u(H)C_u$ | $C_u$ | -0.64574          | -1.13379          | 0                 | 0                 | -153.39522                          | 0.91771                      | -16.0528                            | -16.41442            | 90.51                  | 89.49                   | 42.40                   | 1.33953         | 0.00729         |
| $C_u(H)C_u - C_u(H)C_u$ | $C_u$ | -0.64574          | -1.13379          | 0                 | 0                 | -153.39522                          | 0.91771                      | -16.0528                            | -16.41442            | 137.29                 | 42.71                   | 61.04                   | 0.70255         | 0.60208         |
| $C_u(H)C_u = C_iN$      | $C_u$ | -1.13379          | -0.60631          | 0                 | 0                 | -153.35580                          | 0.91771                      | -16.56586                           | -16.37500            | 137.37                 | 42.63                   | 61.14                   | 0.70038         | 0.60425         |
| $C_iC_u - NC_u$         | $C_u$ | -1.13379          | -0.60631          | 0                 | 0                 | -153.35580                          | 0.91771                      | -16.56586                           | -16.37500            | 138.03                 | 41.97                   | 61.42                   | 0.69080         | 0.61064         |
| $C_iC_u - NC_u$         | N     | -0.60631          | -0.60631          | 0                 | 0                 |                                     | 0.93084                      | -16.03838                           |                      | 139.04                 | 40.96                   | 62.76                   | 0.66083         | 0.64061         |
| $C_iC_u - NC_u$         | N     | -0.60631          | -0.60631          | 0                 | 0                 |                                     | 0.93084                      | -16.03838                           |                      | 119.52                 | 60.48                   | 65.13                   | 0.52338         | 0.41796         |
| $N-H(NH)$               | $C_u$ | -0.60631          | -0.85035          | -0.60631          | 0                 | -153.92269                          | 0.91771                      | -17.13276                           | -16.94189            | 136.97                 | 43.03                   | 60.05                   | 0.72095         | 0.58048         |

Table 15.324. The energy parameters (eV) of functional groups of indole.

| Parameters                         | C=C Group  | CH (i) Group   | C=C Group  | C-C Group | CH (ii) Group | C-N-C Group | NH Group  |
|------------------------------------|------------|----------------|------------|-----------|---------------|-------------|-----------|
| $f_1$                              | 0.75       | 1              | 1          | 1         | 1             | 1           | 1         |
| $n_1$                              | 2          | 1              | 2          | 1         | 1             | 2           | 1         |
| $n_2$                              | 0          | 0              | 0          | 0         | 0             | 0           | 0         |
| $n_3$                              | 0          | 0              | 0          | 0         | 0             | 0           | 0         |
| $C_1$                              | 0.5        | 0.75           | 0.5        | 0.5       | 0.75          | 0.5         | 0.75      |
| $C_2$                              | 0.85252    | 1              | 0.85252    | 1         | 1             | 0.85252     | 0.93613   |
| $C_3$                              | 1          | 1              | 1          | 1         | 1             | 1           | 0.75      |
| $C_4$                              | 0.85252    | 0.91771        | 0.85252    | 0.85252   | 0.91771       | 0.84665     | 0.92171   |
| $C_5$                              | 0          | 1              | 0          | 0         | 1             | 0           | 1         |
| $C_6$                              | 3          | 1              | 4          | 2         | 1             | 4           | 1         |
| $C_7$                              | 0          | 1              | 0          | 0         | 1             | 0           | 1         |
| $C_{100}$                          | 0.5        | 0.75           | 0.5        | 0.5       | 0.75          | 0.5         | 0.75      |
| $C_{200}$                          | 0.85252    | 1              | 0.85252    | 1         | 1             | 0.85252     | 1         |
| $V_1$ (eV)                         | -101.12679 | -37.10024      | -104.37986 | -32.93291 | -39.09538     | -104.73877  | -39.48897 |
| $V_2$ (eV)                         | 20.69825   | 13.17125       | 20.85777   | 10.10210  | 13.45505      | 20.90891    | 14.45367  |
| $T$ (eV)                           | 34.31559   | 11.58941       | 35.96751   | 9.07768   | 12.74462      | 36.26840    | 15.88820  |
| $V_m$ (eV)                         | -17.15779  | -5.79470       | -17.98376  | -4.53884  | -6.37231      | -18.13420   | -7.93410  |
| $E_1$ (eV)                         | 0          | -14.63489      | 0          | -14.63489 | -14.63489     | 0           | -14.53414 |
| $\Delta E_{H_{100}}(s, s, m)$ (eV) | 0          | -1.13379       | -2.26759   | -1.29147  | -2.26758      | -2.42526    | 0         |
| $E_2$ (eV)                         | 0          | -13.50110      | 2.26759    | -13.34342 | -12.36731     | 2.42526     | -14.53414 |
| $E_3$ (eV)                         | -63.27075  | -31.63539      | -63.27075  | -31.63539 | -31.63533     | -63.27040   | -31.63534 |
| $E_4$ (eV)                         | -2.26759   | -0.56690       | -2.26759   | -1.29147  | 0             | -2.42526    | 0         |
| $E_5$ (eV)                         | -65.53833  | -32.20226      | -65.53833  | -32.92684 | -31.63537     | -65.69600   | -31.63537 |
| $\omega$ ( $10^5$ rad/s)           | 49.7272    | 26.4826        | 15.4421    | 21.8249   | 28.9084       | 54.5632     | 48.7771   |
| $E_6$ (eV)                         | 32.73133   | 17.43132       | 10.16428   | 14.36554  | 19.02803      | 35.91442    | 32.10594  |
| $E_7$ (eV)                         | -0.35806   | -0.26130       | -0.20668   | -0.24690  | -0.27301      | -0.38945    | -0.35462  |
| $E_8$ (eV)                         | 0.19649    | 0.35532        | 0.17897    | 0.12312   | 0.39427       | 0.11159     | 0.40696   |
| $E_9$ (eV)                         | [49]       | $E_9$ (13.458) | [6]        | [2]       | [56]          | [12]        | [24]      |
| $E_{100}$ (eV)                     | -0.25982   | -0.08364       | -0.11720   | -0.18534  | -0.07587      | -0.33365    | -0.15115  |
| $E_{1000}$ (eV)                    | 0.14803    | 0.14803        | 0.14803    | 0.14803   | 0.14803       | 0.14803     | 0.14803   |
| $E_{10000}$ (eV)                   | -49.54347  | -32.28590      | -65.77272  | -33.11218 | -31.71124     | -66.36330   | -31.78651 |
| $E_{100000}$ (eV)                  | -14.63489  | -14.63489      | -14.63489  | -14.63489 | -14.63489     | -14.63489   | -14.63489 |
| $E_{1000000}$ (eV)                 | 0          | -13.59844      | 0          | 0         | -13.59844     | 0           | -13.59844 |
| $E_{10000000}$ (eV)                | 5.63881    | 3.90454        | 7.23317    | 3.84240   | 3.32988       | 7.82374     | 3.51208   |



Table 15.325. The total bond energies of indole calculated using the functional group composition and the energies of Table 15.324 compared to the experimental values [2].

| Formula                         | Name   | $\nu$<br>C=C | CH (i) | C=C | C-C | CH (ii) | C-N-C | NH | Calculated<br>Total Bond Energy<br>(eV) | Experimental<br>Total Bond Energy<br>(eV) | Relative Error |
|---------------------------------|--------|--------------|--------|-----|-----|---------|-------|----|-----------------------------------------|-------------------------------------------|----------------|
| C <sub>8</sub> H <sub>7</sub> N | Indole | 6            | 4      | 1   | 1   | 2       | 1     | 1  | 78.3215                                 | 78.314                                    | -0.00010       |

Table 15.326. The bond angle parameters of indole and experimental values [1]. In the calculation of  $\theta_v$ , the parameters from the preceding angle were used.  $E_T$  is  $E_T(\text{atom} - \text{atom}, \text{usp}^3 \text{AO})$ .

| Atoms of Angle               | $2c^1$<br>Bond 1<br>( $a_1$ ) | $2c^1$<br>Bond 2<br>( $a_1$ ) | $2c^1$<br>Terminal<br>Atom<br>( $a_1$ ) | $E_{\text{conductor}}$<br>Atom 1 | Atom 1<br>Hybridization<br>Designation<br>(Table 15.3B) | $E_{\text{conductor}}$<br>Atom 2 | Atom 2<br>Hybridization<br>Designation<br>(Table 15.3B) | $c_2$<br>Atom 1 | $c_2$<br>Atom 2 | $C_1$ | $C_2$ | $c_1$ | $c_1'$  | $E_T$<br>(eV) | $\theta_v$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | Cal. $\theta$<br>( $^\circ$ ) | Exp. $\theta$<br>( $^\circ$ ) |
|------------------------------|-------------------------------|-------------------------------|-----------------------------------------|----------------------------------|---------------------------------------------------------|----------------------------------|---------------------------------------------------------|-----------------|-----------------|-------|-------|-------|---------|---------------|----------------------------|----------------------------|----------------------------|-------------------------------|-------------------------------|
| $\angle C'C'C$<br>(aromatic) | 2.62936                       | 2.62936                       | 4.5585                                  | -17.17218                        | 20                                                      | -17.17218                        | 20                                                      | 0.79232         | 0.79232         | 1     | 1     | 1     | 0.79232 | -1.85336      |                            |                            |                            | 120.19                        | 120 [50-52]<br>(benzene)      |
| $\angle C'CH$<br>(aromatic)  |                               |                               |                                         |                                  |                                                         |                                  |                                                         |                 |                 |       |       |       |         |               |                            | 120.19                     |                            | 119.91                        | 120 [50-52]<br>(benzene)      |

## ADENINE

Adenine having the formula  $C_5H_5N_5$  comprises a pyrimidine moiety with an aniline group and a conjugated five-membered ring which comprises imidazole except that one of the double bonds is part of the aromatic ring. The structure is shown in Figure. 75. The aromatic  $C=C$ ,  $C-H$ , and  $C=N$  functional groups of the pyrimidine moiety are equivalent to those of pyrimidine as given in the corresponding section. The  $NH_2$  and  $C_a-N_a$  functional groups of the aniline moiety are equivalent to those of aniline as given in the corresponding section. The  $CH$ ,  $NH$ ,  $C_d-N_e$ , and  $N_e=C_e$  groups of the imidazole-type ring are equivalent to the corresponding groups of imidazole as given in the corresponding section. The  $C-N-C$  functional group of the imidazole-type ring is equivalent to the corresponding group of indole having the same structure with the  $C-N-C$  group bonding to aryl and alkenyl groups.

The symbols of the functional groups of adenine are given in Table 15.327. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of adenine are given in Tables 15.328, 15.329, and 15.330, respectively. The total energy of adenine given in Table 15.332 was calculated as the sum over the integer multiple of each  $E_D(\text{Group})$  of Table 15.330 corresponding to functional-group composition of the molecule. The bond angle parameters of adenine determined using Eqs. (15.79-15.108) are given in Table 15.332.

Table 15.327. The symbols of functional groups of adenine.

| Functional Group                      | Group Symbol |
|---------------------------------------|--------------|
| $CC$ (aromatic bond)                  | $C=C$        |
| $CH$ (aromatic)                       | $CH$ (i)     |
| $C_{b,c}^{3e}=N_c$ $C_{a,b}^{3e}=N_b$ | $C=N$        |
| $C_a-N_a$                             | $C-N$ (a)    |
| $NH_2$ group                          | $NH_2$       |
| $N_e=C_e$ double bond                 | $N=C$        |
| $C_d-N_e$                             | $C-N$ (b)    |
| $N_dH$ group                          | $NH$         |
| $CH$                                  | $CH$ (ii)    |
| $C_c-N_d-C_e$                         | $C-N-C$      |

Table 15.328. The geometrical bond parameters of adenine and experimental values [1].

| Parameter                | C=C Group             | CH (i) Group        | C=N Group             | C-N (a) Group      | NH <sub>2</sub> Group | N=C Group | C-N (b) Group | NH Group           | CH (ii) Group      | C-N-C Group        |
|--------------------------|-----------------------|---------------------|-----------------------|--------------------|-----------------------|-----------|---------------|--------------------|--------------------|--------------------|
| $a$ ( $a_0$ )            | 1.47348               | 1.60061             | 1.47169               | 1.81158            | 1.24428               | 1.44926   | 1.82450       | 1.24428            | 1.53380            | 1.44394            |
| $c'$ ( $a_0$ )           | 1.31468               | 1.03299             | 1.27073               | 1.34595            | 0.94134               | 1.30383   | 1.35074       | 0.94134            | 1.01120            | 1.30144            |
| Bond Length<br>$2c'$ (Å) | 1.39140               | 1.09327             | 1.34489               | 1.42449            | 0.99627               | 1.37991   | 1.42956       | 0.996270           | 1.07021            | 1.37738            |
| Exp. Bond Length<br>(Å)  | 1.393<br>(pyrimidine) | 1.084<br>(pyridine) | 1.340<br>(pyrimidine) | 1.431<br>(aniline) | 0.998<br>(aniline)    |           |               | 0.996<br>(pyrrole) | 1.076<br>(pyrrole) | 1.370<br>(pyrrole) |
| $h.c$ ( $a_0$ )          | 0.66540               | 1.22265             | 0.74237               | 1.21254            | 0.81370               | 0.63276   | 1.22650       | 0.81370            | 1.15326            | 0.62548            |
| $e$                      | 0.89223               | 0.64537             | 0.86345               | 0.74297            | 0.75653               | 0.89565   | 0.74033       | 0.75653            | 0.65928            | 0.90131            |

Table 15.329. The MO to HO intercept geometrical bond parameters of adenine.  $R_i$  is an alkyl group and  $R, R', R''$  are H or alkyl groups.  $E_i$  is  $E_i(\text{atom} - \text{atom}, \text{exp}, \Delta O)$ .

| Bond                                                                         | Atom  | $E_T$<br>(eV)<br>Bond 1 | $E_T$<br>(eV)<br>Bond 2 | $E_T$<br>(eV)<br>Bond 3 | $E_T$<br>(eV)<br>Bond 4 | Final Total<br>Energy<br>$C2sp^2$<br>(eV) | $r_{\text{final}}$<br>( $a_0$ ) | $E_{\text{bond}}(C2sp^2)$<br>(eV)<br>Final | $E(C2sp^2)$<br>(eV)<br>Final | $\theta^*$<br>(°) | $\theta_i$<br>(°) | $\theta_j$<br>(°) | $d_i$<br>( $a_0$ ) | $d_j$<br>( $a_0$ ) |
|------------------------------------------------------------------------------|-------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------------------------|---------------------------------|--------------------------------------------|------------------------------|-------------------|-------------------|-------------------|--------------------|--------------------|
| $C_1(N_1)C_2(N_2)H-H$                                                        | $N_1$ | -0.56090                | 0                       | 0                       | 0                       | -153.57636                                | 0.93084                         | -15.39765                                  | -15.39765                    | 121.74            | 58.26             | 67.49             | 0.47034            | 0.46500            |
| $C_2(N_2)C_3(N_3)H_2$                                                        | $C_2$ | -0.56090                | -0.54343                | -0.83035                | 0                       | -153.57636                                | 0.91771                         | -16.78642                                  | -16.78642                    | 89.90             | 90.10             | 41.95             | 1.34737            | 0.00142            |
| $C_2(N_2)C_3(N_3)H_2$                                                        | $N_2$ | -0.56090                | 0                       | 0                       | 0                       | -153.57636                                | 0.93084                         | -15.39765                                  | -15.39765                    | 96.32             | 83.68             | 46.43             | 1.28839            | 0.09756            |
| $C_3(N_3)C_4(N_4)H$                                                          | $C_3$ | -0.54343                | -0.54343                | -0.56690                | 0                       | -153.26945                                | 0.91771                         | -16.47951                                  | -16.28864                    | 78.27             | 101.73            | 41.39             | 1.20084            | 0.16785            |
| $C_3(N_3)C_4(N_4)H$                                                          | $C_4$ | -0.92018                | -0.60631                | 0                       | 0                       | -153.15119                                | 0.91771                         | -16.36125                                  | -16.17038                    | 79.01             | 100.29            | 41.89             | 1.19199            | 0.15860            |
| $N-H$                                                                        | $N$   | -0.60631                | -0.60631                | 0                       | 0                       | -153.15119                                | 0.93084                         | -16.03838                                  | -16.03838                    | 119.52            | 60.48             | 65.13             | 0.32338            | 0.41796            |
| $C_5(N_5)C_6(N_6)H$                                                          | $C_5$ | -0.83035                | -0.54343                | -0.56690                | 0                       | -153.57636                                | 0.91771                         | -16.78642                                  | -16.59556                    | 128.54            | 51.46             | 58.65             | 0.76572            | 0.50001            |
| $C_5(N_5)C_6(N_6)H$                                                          | $N_5$ | -0.54343                | -0.54343                | 0                       | 0                       | -153.57636                                | 0.93084                         | -15.91561                                  | -15.91561                    | 130.61            | 49.39             | 60.97             | 0.71418            | 0.35656            |
| $N_5C_5=N_6C_6$                                                              | $N_6$ | -0.54343                | -0.54343                | -0.56690                | 0                       | -153.26945                                | 0.91771                         | -16.47951                                  | -16.28865                    | 129.26            | 50.74             | 59.44             | 0.74824            | 0.32249            |
| $C_6(N_6)C_7(N_7)H$                                                          | $C_6$ | -0.83035                | -0.54343                | -0.60631                | 0                       | -153.61578                                | 0.91771                         | -16.82384                                  | -16.63498                    | 128.45            | 51.55             | 58.55             | 0.76792            | 0.50281            |
| $C_6(N_6)C_7(N_7)H$                                                          | $C_7$ | -0.83035                | -0.54343                | -0.56690                | 0                       | -153.57636                                | 0.91771                         | -16.78642                                  | -16.59556                    | 134.85            | 43.15             | 59.72             | 0.74304            | 0.57165            |
| $N_6(N_6)C_7(N_7)C_8(N_8)C_9(N_9)C_{10}(N_{10})C_{11}(N_{11})C_{12}(N_{12})$ | $C_8$ | -0.83035                | -0.83035                | -0.46459                | 0                       | -153.78097                                | 0.91771                         | -16.09103                                  | -16.80017                    | 134.44            | 45.56             | 59.22             | 0.75598            | 0.56071            |
| $C_8(N_8)C_9(N_9)C_{10}(N_{10})C_{11}(N_{11})C_{12}(N_{12})$                 | $C_9$ | -0.83035                | -0.54343                | -0.60631                | 0                       | -153.61578                                | 0.91771                         | -16.82384                                  | -16.63498                    | 134.77            | 45.23             | 59.62             | 0.74516            | 0.56952            |
| $C_8(N_8)C_9(N_9)C_{10}(N_{10})C_{11}(N_{11})C_{12}(N_{12})$                 | $C_9$ | -0.83035                | -0.54343                | -0.60631                | 0                       | -153.61578                                | 0.91771                         | -16.82384                                  | -16.63498                    | 137.54            | 42.46             | 60.78             | 0.70488            | 0.59656            |
| $N_6(N_6)C_7(N_7)C_8(N_8)C_9(N_9)C_{10}(N_{10})C_{11}(N_{11})C_{12}(N_{12})$ | $N_6$ | -0.60631                | -0.60631                | 0                       | 0                       | -153.78097                                | 0.93084                         | -16.03838                                  | -16.03838                    | 139.04            | 40.96             | 62.76             | 0.66083            | 0.64661            |
| $C_8(N_8)C_9(N_9)C_{10}(N_{10})C_{11}(N_{11})C_{12}(N_{12})$                 | $C_8$ | -0.60631                | -0.92018                | 0                       | 0                       | -153.15119                                | 0.91771                         | -16.36125                                  | -16.17039                    | 138.42            | 41.58             | 61.93             | 0.67940            | 0.62303            |
| $C_8(N_8)C_9(N_9)C_{10}(N_{10})C_{11}(N_{11})C_{12}(N_{12})$                 | $C_9$ | -0.92018                | -0.60631                | 0                       | 0                       | -153.15119                                | 0.91771                         | -16.36125                                  | -16.17039                    | 137.93            | 42.07             | 61.72             | 0.68657            | 0.61726            |
| $C_8(N_8)C_9(N_9)C_{10}(N_{10})C_{11}(N_{11})C_{12}(N_{12})$                 | $N_6$ | -0.92018                | -0.46459                | 0                       | 0                       | -153.78097                                | 0.93084                         | -16.21952                                  | -16.21952                    | 138.20            | 41.80             | 62.08             | 0.67849            | 0.62534            |
| $C_8(N_8)C_9(N_9)C_{10}(N_{10})C_{11}(N_{11})C_{12}(N_{12})$                 | $N_6$ | -0.46459                | -0.92018                | 0                       | 0                       | -153.78097                                | 0.93084                         | -16.21952                                  | -16.21952                    | 91.32             | 88.68             | 43.14             | 1.33135            | 0.01939            |
| $C_8(N_8)C_9(N_9)C_{10}(N_{10})C_{11}(N_{11})C_{12}(N_{12})$                 | $C_9$ | -0.46459                | -0.83035                | -0.83035                | 0                       | -153.78097                                | 0.91771                         | -16.99103                                  | -16.80017                    | 87.71             | 92.29             | 40.72             | 1.38280            | 0.03206            |

Table 15.330. The energy parameters (eV) of functional groups of adenine.

| Parameters                | $\overset{+}{C}=\overset{+}{C}$<br>Group | $\overset{+}{C}H$ (i)<br>Group | $\overset{+}{C}=\overset{+}{N}$<br>Group | $\overset{+}{C}-N$ (a)<br>Group | $NH_2$<br>Group | $N=C$<br>Group | $\overset{+}{C}-N$ (b)<br>Group | $NH$<br>Group | $\overset{+}{C}H$ (ii)<br>Group | $\overset{+}{C}-N-\overset{+}{C}$<br>Group |
|---------------------------|------------------------------------------|--------------------------------|------------------------------------------|---------------------------------|-----------------|----------------|---------------------------------|---------------|---------------------------------|--------------------------------------------|
| $f_1$                     | 0.75                                     | 1                              | 1                                        | 1                               | 1               | 1              | 1                               | 1             | 1                               | 1                                          |
| $f_2$                     | 2                                        | 1                              | 2                                        | 1                               | 2               | 2              | 1                               | 1             | 1                               | 2                                          |
| $f_3$                     | 0                                        | 0                              | 0                                        | 0                               | 0               | 0              | 0                               | 0             | 0                               | 0                                          |
| $f_4$                     | 0                                        | 0                              | 0                                        | 0                               | 1               | 0              | 0                               | 0             | 0                               | 0                                          |
| $C_1$                     | 0.5                                      | 0.75                           | 0.5                                      | 0.5                             | 0.75            | 0.5            | 0.5                             | 0.75          | 0.75                            | 0.5                                        |
| $C_2$                     | 0.85252                                  | 1                              | 0.91140                                  | 1                               | 0.93613         | 0.85252        | 1                               | 0.93613       | 1                               | 0.85252                                    |
| $C_3$                     | 1                                        | 1                              | 1                                        | 1                               | 0.75            | 1              | 1                               | 0.75          | 1                               | 1                                          |
| $C_4$                     | 0.85252                                  | 0.91771                        | 0.91140                                  | 0.84665                         | 0.92171         | 0.84665        | 0.84665                         | 0.92171       | 0.91771                         | 0.84665                                    |
| $C_5$                     | 0                                        | 1                              | 0                                        | 0                               | 0               | 0              | 0                               | 1             | 1                               | 0                                          |
| $C_6$                     | 3                                        | 1                              | 3                                        | 2                               | 1               | 4              | 2                               | 1             | 1                               | 4                                          |
| $C_7$                     | 0                                        | 1                              | 0                                        | 0                               | 2               | 0              | 0                               | 1             | 1                               | 0                                          |
| $C_{10}$                  | 0.5                                      | 0.75                           | 0.5                                      | 0.5                             | 1.5             | 0.5            | 0.5                             | 0.75          | 0.75                            | 0.5                                        |
| $C_{10a}$                 | 0.85252                                  | 1                              | 0.91140                                  | 1                               | 1               | 0.85252        | 1                               | 1             | 1                               | 0.85252                                    |
| $V_2$ (eV)                | -101.12679                               | -37.10024                      | -102.01431                               | -32.76465                       | -78.97795       | -103.92756     | -32.44864                       | -39.48897     | -39.09538                       | -104.73877                                 |
| $V_3$ (eV)                | 20.69825                                 | 13.17125                       | 21.41410                                 | 10.10870                        | 28.90735        | 20.87050       | 10.07285                        | 14.45367      | 13.45505                        | 20.90891                                   |
| $T$ (eV)                  | 34.31559                                 | 11.58941                       | 34.65890                                 | 9.04312                         | 31.73641        | 35.85539       | 8.89248                         | 15.86820      | 12.74462                        | 36.20840                                   |
| $V_m$ (eV)                | -17.15779                                | -5.79470                       | -17.32945                                | -4.52156                        | -15.86820       | -17.92770      | -4.44624                        | -7.93410      | -6.37231                        | -18.13420                                  |
| $E_{10a}$ (eV)            | 0                                        | -14.63489                      | 0                                        | -14.63489                       | -14.53414       | 0              | -14.63489                       | -14.53414     | -14.63489                       | 0                                          |
| $\Delta E_{10a,10b}$ (eV) | 0                                        | -1.13379                       | 0                                        | -1.13379                        | 0               | -1.85836       | -0.92918                        | 0             | -2.26758                        | -2.42526                                   |
| $E_{10b}$ (eV)            | 0                                        | -13.50110                      | 0                                        | -13.50110                       | -14.53414       | 1.85836        | -13.70571                       | -14.53414     | -12.36731                       | 2.42526                                    |
| $E_{10c}$ (eV)            | 0                                        | 0                              | 0                                        | 0                               | -14.53414       | 0              | 0                               | 0             | 0                               | 0                                          |
| $E_{10d}$ (eV)            | -63.27075                                | -31.63539                      | -63.27076                                | -31.63549                       | -48.73654       | -63.27100      | -31.63527                       | -31.63534     | -31.63553                       | -63.27040                                  |
| $E_{10e}$ (eV)            | -2.26759                                 | -0.56690                       | -1.44915                                 | -1.13379                        | 0               | -1.85836       | -0.92918                        | 0             | 0                               | -2.42526                                   |
| $E_{10f}$ (eV)            | -65.53833                                | -32.20226                      | -64.71988                                | -32.76916                       | -48.73660       | -65.12910      | -32.56455                       | -31.63557     | -31.63557                       | -65.69600                                  |
| $\omega$ ( $10^3$ rad/s)  | 49.7272                                  | 26.4826                        | 43.6311                                  | 11.9890                         | 68.9812         | 15.4704        | 21.5213                         | 48.7771       | 28.9084                         | 54.5632                                    |
| $E_{10g}$ (eV)            | 32.73133                                 | 17.43132                       | 28.71875                                 | 7.89138                         | 45.40465        | 10.18290       | 14.16571                        | 32.10594      | 19.02803                        | 35.91442                                   |
| $E_{10h}$ (eV)            | -0.35806                                 | -0.26130                       | -0.33540                                 | -0.18211                        | -0.42172        | -0.20558       | -0.24248                        | -0.35462      | -0.27301                        | -0.38945                                   |
| $E_{10i}$ (eV)            | 0.19649                                  | 0.35532                        | 0.19649                                  | 0.15498                         | 0.40929         | 0.20768        | 0.12944                         | 0.40696       | 0.39427                         | 0.11159                                    |
| $E_{10j}$ (eV)            | [49]                                     | $E_0$ (13.458)                 | [49]                                     | [54]                            | [22]            | [58]           | [23]                            | [24]          | [56]                            | [12]                                       |
| $E_{10k}$ (eV)            | -0.25982                                 | -0.08364                       | -0.23715                                 | -0.10462                        | -0.21708        | -0.10174       | -0.17775                        | -0.15115      | -0.07587                        | -0.33365                                   |
| $E_{10l}$ (eV)            | 0.14803                                  | 0.14803                        | 0.09457                                  | 0.14803                         | 0.14803         | 0.14803        | 0.14803                         | 0.14803       | 0.14803                         | 0.14803                                    |
| $E_{10m}$ (eV)            | -49.54347                                | -32.38590                      | -48.82472                                | -32.87379                       | -49.17075       | -65.33259      | -32.74230                       | -31.78651     | -31.71124                       | -66.36330                                  |
| $E_{10n}$ (eV)            | -14.63489                                | -14.63489                      | -14.63489                                | -14.63489                       | -14.53414       | -14.63489      | -14.63489                       | -14.53414     | -14.63489                       | -14.63489                                  |
| $E_{10o}$ (eV)            | 0                                        | -13.59844                      | 0                                        | 0                               | -13.59844       | 0              | 0                               | -13.59844     | -13.59844                       | 0                                          |
| $E_{10p}$ (eV)            | 5.63881                                  | 3.90454                        | 4.92005                                  | 3.60401                         | 7.43973         | 6.79303        | 3.47253                         | 3.51208       | 3.32988                         | 7.82374                                    |

Table 15.331. The total bond energies of adenine calculated using the functional group composition and the energies of Table 15.330 compared to the experimental values [2].

| Formula     | Name    | $\overset{+}{C}=\overset{+}{C}$ | $\overset{+}{C}H$ (i) | $\overset{+}{C}=\overset{+}{N}$ | $\overset{+}{C}-N$ (a) | $NH_2$ | $N=C$ | $\overset{+}{C}-N$ (b) | $NH$ | $\overset{+}{C}H$ (ii) | $\overset{+}{C}-N-\overset{+}{C}$ | Calculated<br>Total Bond Energy<br>(eV) | Experimental<br>Total Bond Energy<br>(eV) | Relative Error |
|-------------|---------|---------------------------------|-----------------------|---------------------------------|------------------------|--------|-------|------------------------|------|------------------------|-----------------------------------|-----------------------------------------|-------------------------------------------|----------------|
| $C_4H_4N_6$ | Adenine | 2                               | 1                     | 1                               | 1                      | 1      | 1     | 1                      | 1    | 1                      | 1                                 | 70.8375                                 | 70.7981                                   | -0.00055       |

Table 15.332. The bond angle parameters of adenine and experimental values [61]. In the calculation of  $\theta_r$ , the parameters from the preceding angle were used.  $E_r$  is  $E_T(atom - atom, msp, AO)$ .

| Atoms of Angle   | $\angle C_1$<br>Bond 1<br>( $a_1$ ) | $\angle C_2$<br>Bond 2<br>( $a_2$ ) | $\angle C_3$<br>Terminated<br>Atom<br>( $a_3$ ) | $E_r$<br>Terminated<br>Atom 1<br>( $a_1$ ) | Atom 1<br>Hybridization<br>Designation<br>(Table 15.3B) | $E_r$<br>Terminated<br>Atom 2<br>( $a_2$ ) | Atom 2<br>Hybridization<br>Designation<br>(Table 15.3B) | $c_1$<br>Atom 1              | $c_2$<br>Atom 2              | $C_1$ | $C_2$ | $C_3$ | $c_1$ | $c_2$   | $E_r$<br>(eV) | $\theta_r$<br>( $^\circ$ ) | $\theta_1$<br>( $^\circ$ ) | $\theta_2$<br>( $^\circ$ ) | Cal. $\theta$<br>( $^\circ$ ) | Exp. $\theta$<br>( $^\circ$ ) |
|------------------|-------------------------------------|-------------------------------------|-------------------------------------------------|--------------------------------------------|---------------------------------------------------------|--------------------------------------------|---------------------------------------------------------|------------------------------|------------------------------|-------|-------|-------|-------|---------|---------------|----------------------------|----------------------------|----------------------------|-------------------------------|-------------------------------|
| $\angle HNH$     | 1.88268                             | 1.88268                             | 3.1539                                          | -14.53414                                  | N                                                       | H                                          | H                                                       | 0.95613<br>(Eq.<br>(15.248)) | 1                            | 1     | 1     | 1     | 0.75  | 1.06823 | 0             |                            |                            |                            | 113.89                        | 113.9 [1]<br>(equiline)       |
| $\angle HNC$     | 1.88268                             | 2.69190                             | 4.0497                                          | -14.53414                                  | N                                                       | -15.95955                                  | 6                                                       | 0.84665<br>(Eq.<br>(15.152)) | 0.84665<br>(Eq.<br>(15.152)) | 0.75  | 1     | 1     | 0.75  | 1.01912 | 0             |                            |                            |                            | 123.60                        | 118                           |
| $\angle H_C N_C$ | 2.06598                             | 2.54147                             | 3.9497                                          | -14.52575                                  | I                                                       | -14.53414                                  | N                                                       | 0.91771<br>(Eq.<br>(15.116)) | 0.91771<br>(Eq.<br>(15.116)) | 0.75  | 1     | 1     | 0.75  | 0.99312 | 0             |                            |                            |                            | 117.65                        | 115<br>116                    |
| $\angle H_C N_C$ | 2.02241                             | 2.60766                             | 4.0661                                          | -16.36125                                  | 10                                                      | -14.53414                                  | N                                                       | 0.83159<br>(Eq.<br>(15.152)) | 0.83159<br>(Eq.<br>(15.152)) | 0.75  | 1     | 1     | 0.75  | 1.01811 | 0             |                            |                            |                            | 122.35                        | 126                           |
| $\angle H_C N_C$ |                                     |                                     |                                                 |                                            |                                                         |                                            |                                                         |                              |                              |       |       |       |       |         |               |                            | 122.35                     | 112.64                     | 125.02                        | 119                           |
| $\angle H_C N_C$ | 1.88268                             | 2.60287                             | 4.0497                                          | -14.53414                                  | N                                                       | -15.95955                                  | 6                                                       | 0.84665<br>(Eq.<br>(15.152)) | 0.84665<br>(Eq.<br>(15.152)) | 0.75  | 1     | 1     | 0.75  | 1.01912 | 0             |                            |                            |                            | 128.35                        | 127                           |
| $\angle H_C N_C$ | 2.60766                             | 2.60287                             | 4.3359                                          | -16.21952                                  | 8                                                       | -16.03838                                  | 7                                                       | 0.83885<br>(Eq.<br>(15.116)) | 0.84833<br>(Eq.<br>(15.152)) | 1     | 1     | 1     | 1     | 0.84359 | -1.44915      |                            |                            |                            | 112.64                        | 114.4                         |
| $\angle N_C N_C$ | 2.54147                             | 2.60287                             | 4.6260                                          | -14.53414                                  | N                                                       | -14.53414                                  | N                                                       | 0.91140<br>(Eq.<br>(15.116)) | 0.84665<br>(Eq.<br>(15.152)) | 1     | 1     | 1     | 1     | 0.87902 | -1.44915      |                            |                            |                            | 128.11                        | 127.8                         |
| $\angle N_C N_C$ | 2.54147                             | 2.54147                             | 4.5826                                          | -15.55033                                  | 3                                                       | -15.55033                                  | 3                                                       | 0.87495<br>(Eq.<br>(15.152)) | 0.87495<br>(Eq.<br>(15.152)) | 1     | 1     | 1     | 1     | 0.87495 | -1.44915      |                            |                            |                            | 128.75                        | 128.9                         |
| $\angle N_C N_C$ | 2.54147                             | 2.69190                             | 4.5826                                          | -15.91261                                  | 5                                                       | -15.39265                                  | 2                                                       | 0.85303<br>(Eq.<br>(15.152)) | 0.88392<br>(Eq.<br>(15.152)) | 1     | 1     | 1     | 1     | 0.86947 | -1.44915      |                            |                            |                            | 122.22                        | 119.7                         |
| $\angle N_C C_C$ | 2.70148                             | 2.62936                             | 4.3818                                          | -14.53414                                  | N                                                       | -14.53414                                  | 6                                                       | 0.84665<br>(Eq.<br>(15.152)) | 0.85252<br>(Eq.<br>(15.152)) | 1     | 1     | 1     | 1     | 0.84958 | -1.44915      |                            |                            |                            | 110.56                        | 110.4                         |
| $\angle N_C C_C$ | 2.60287                             | 2.62936                             | 4.1952                                          | -14.53414                                  | N                                                       | -16.99103                                  | 16                                                      | 0.84665<br>(Eq.<br>(15.152)) | 0.80076<br>(Eq.<br>(15.152)) | 1     | 1     | 1     | 1     | 0.82371 | -1.44915      |                            |                            |                            | 106.60                        | 105.9                         |
| $\angle N_C C_C$ | 2.54147                             | 2.62936                             | 4.4721                                          | -14.53414                                  | N                                                       | -16.99103                                  | 16                                                      | 0.91140<br>(Eq.<br>(15.116)) | 0.80076<br>(Eq.<br>(15.152)) | 1     | 1     | 1     | 1     | 0.85608 | -1.44915      |                            |                            |                            | 110.73                        | 126.4                         |
| $\angle N_C C_C$ | 2.54147                             | 2.62936                             | 4.4721                                          | -14.53414                                  | N                                                       | -16.99103                                  | 16                                                      | 0.91140<br>(Eq.<br>(15.116)) | 0.80076<br>(Eq.<br>(15.152)) | 1     | 1     | 1     | 1     | 0.85608 | -1.44915      |                            |                            |                            | 110.73                        | 118.2                         |
| $\angle N_C C_C$ | 2.69190                             | 2.62936                             | 4.5607                                          | -14.53414                                  | N                                                       | -16.52644                                  | 12                                                      | 0.91140<br>(Eq.<br>(15.116)) | 0.83327<br>(Eq.<br>(15.116)) | 1     | 1     | 1     | 1     | 0.86734 | -1.44915      |                            |                            |                            | 117.97                        | 122.1                         |
| $\angle N_C C_C$ | 2.70148                             | 2.62936                             | 4.8990                                          | -14.53414                                  | N                                                       | -14.82575                                  | 1                                                       | 0.91140<br>(Eq.<br>(15.116)) | 0.91771<br>(Eq.<br>(15.116)) | 1     | 1     | 1     | 1     | 0.91456 | -1.44915      |                            |                            |                            | 133.55                        | 132.8                         |
| $\angle C_C N_C$ | 2.70148                             | 2.60766                             | 4.2661                                          | -17.92022                                  | 28                                                      | -17.92022                                  | 28                                                      | 0.75924<br>(Eq.<br>(15.152)) | 0.75924<br>(Eq.<br>(15.152)) | 1     | 1     | 1     | 1     | 0.75924 | -1.85836      |                            |                            |                            | 106.93                        | 103.5                         |
| $\angle C_C N_C$ | 2.60287                             | 2.60287                             | 4.2661                                          | -17.75502                                  | 25                                                      | -17.75502                                  | 25                                                      | 0.76631<br>(Eq.<br>(15.152)) | 0.76631<br>(Eq.<br>(15.152)) | 1     | 1     | 1     | 1     | 0.76631 | -1.85836      |                            |                            |                            | 110.07                        | 106.1                         |
| $\angle C_C N_C$ | 2.54147                             | 2.54147                             | 4.3889                                          | -17.40869                                  | 21                                                      | -17.75502                                  | 25                                                      | 0.78155<br>(Eq.<br>(15.152)) | 0.76631<br>(Eq.<br>(15.152)) | 1     | 1     | 1     | 1     | 0.77393 | -1.85836      |                            |                            |                            | 118.09                        | 111.3                         |
| $\angle C_C N_C$ | 2.54147                             | 2.54147                             | 4.3704                                          | -17.71560                                  | 24                                                      | -17.40869                                  | 21                                                      | 0.76801<br>(Eq.<br>(15.152)) | 0.78135<br>(Eq.<br>(15.152)) | 1     | 1     | 1     | 1     | 0.77478 | -1.85836      |                            |                            |                            | 118.59                        | 118.6                         |
| $\angle C_C C_C$ | 2.62936                             | 2.62936                             | 4.4721                                          | -17.71560                                  | 24                                                      | -17.14471                                  | 19                                                      | 0.76801<br>(Eq.<br>(15.152)) | 0.79340<br>(Eq.<br>(15.152)) | 1     | 1     | 1     | 1     | 0.78071 | -1.85836      |                            |                            |                            | 116.52                        | 116.7                         |

838

While the claimed invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one of ordinary skill in the art that various changes and modifications can be made to the claimed invention without departing from the spirit and scope thereof.